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## Thermal Properties of Lignin in Copolymers, Blends, and Composites; A Review

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The need for renewable alternatives to conventional petroleum based polymers has been the motivation for work on biobased composites, blends and materials whose foundations are carbon neutral feedstocks. Lignin, an abundant plant derived feedstock, and waste byproduct of the cellulosic ethanol and pulp and paper industry, qualifies as a renewable material. Despite the fact that it is often difficult to blend lignin with other polymers due to its complex structure and reactivity, published research over the past decade, has focused on issues such as lignin miscibility with other polymers, the thermal and mechanical strength behavior of its copolymers and its fractions as well as efforts of tuning its thermal properties via chemical modifications and other means. As such this effort now attempts to offer a comprehensive overview that largely discusses the importance of these processes with the aim toward effective, cost efficient and environmentally friendly means that may allow the utilization of this important and largely ignored biopolymer.

### Introduction

Organic macromolecules of high molecular weight, which can be easily deformed into any new form when subjected to heat and pressure, are known as plastic or plastic material.<sup>1</sup> In other words, any polymer material that is capable of moulding under pressure and high temperature is considered as a plastic material. Resins are the basic binding materials in plastics which undergoes condensation and polymerization reactions during its preparation.

There are two major classes of polymers based upon their behaviour when exposed to heat; thermoplastics and thermosets. Thermoplastic polymers are the materials that can be softened into a mobile liquid upon the application of heat and return to its solid state when cooled.<sup>2</sup> As such these polymers are generally subjected to injection moulding and extrusion to transform the raw materials to end products. Thermoplastic polymers can be repeatedly softened and re-shaped upon the application of heat.<sup>3-5</sup> These polymers are categorized by configuration of the polymer chains into two types, random state (amorphous) and ordered state (crystalline) (Fig. 1).<sup>6</sup> The distinct properties of thermoplastic polymers include high impact resistance, high reform ability, and ease of recyclability.<sup>6</sup>

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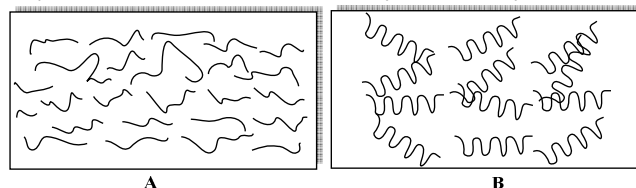
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In contrast to thermoplastic polymers, thermoset polymers are usually malleable before curing that transform into an insoluble infusible three-dimensional cross-linked structure after curing. Thermosets typically are cured and moulded into shape, used as binders and are not recycled as easily.<sup>7</sup>



**Figure 1.** Morphologies of thermoplastic polymers (A) Random state (amorphous) (B) Ordered state (crystalline)

The properties of thermoset resins/polymers include excellent resistance to solvents and corrosives, resistance to heat and high temperature, fatigue strength, tailored elasticity, excellent adhesion, and excellent finishing (polishing, painting, etc.)

**Lignin a natural polymer:** Lignin is the most abundant natural substance composed of aromatic moieties and the second most abundant natural polymer on earth after cellulose.<sup>8-9</sup> This three-dimensional amorphous polymer is primarily found in the vascular plant cell walls in a way “cementing” the cellulose and hemicellulose together. Lignin helps the cell wall and fibres within to transport water and nutrients, protects them from microbial attack, and provides mechanical support.<sup>10-11</sup> It comprises about 30% of the mass of softwoods and 20-25% of hardwood trees.<sup>12</sup>

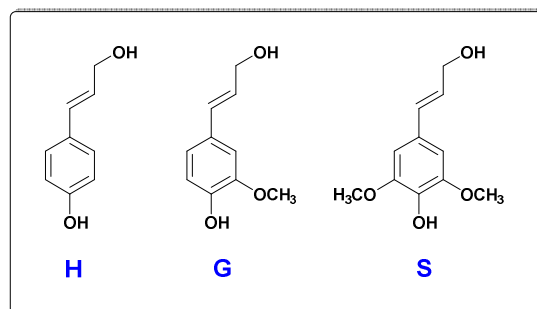
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**Chemical structure of lignin:** The structural unit of lignin is mainly composed of phenyl propane ( $C_6-C_3$ ) units along with phenolic hydroxyl and methoxy substitutions in varying amounts depending on the botanical source of the material. Mainly, three different types of phenyl propane monomer units (also known as monolignols) are present in the lignin backbone. These are namely para-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol, which comprise p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) residues in this natural polymer respectively (Fig. 2).<sup>12-15</sup>



**Figure 2.** Building blocks of lignin p-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) residues

Softwood lignin (mainly obtained from gymnosperms) is generally composed of more than 95% of G units. Hardwood lignin (mainly obtained from angiosperms) is mainly composed of G and S units in varying amounts.<sup>16-18</sup> Whereas, straw, grass and other monocots are mainly composed of H, G, and S units.<sup>10, 18</sup> The other functional groups present in lignin are aliphatic-hydroxyls, carbonyls and carboxyls with varying amounts depending on its origin.<sup>19</sup> The various phenyl propane ( $C_6-C_3$ ) units of lignin are connected by  $\beta$ -O-4, 5-5,  $\beta$ -5, 4-O-5,  $\beta$ -1, dibenzodioxocin, and  $\beta$ - $\beta$  linkages.<sup>20-24</sup> Softwood lignins show comparatively higher glass transition temperatures ( $T_g$  between 138 – 160 °C) most likely due to higher amounts of intermolecular hydrogen bonds and a greater abundance of condensed structure while hardwood lignins show comparatively lower  $T_g$  range ( $T_g$  between 110 – 130 °C).<sup>20</sup> All the reported  $T_g$ s were measured under dry conditions as moisture acts as a plasticizer and changes the  $T_g$  of lignin.

**Classification of lignin based on the extraction procedure:**

The physical and chemical properties of lignin are highly dependent on the pulping process that is used to extract it from the lignocellulosic material. In subsequent parts of this review, we will discuss about lignins obtained via the application of different mechano-chemical routes. Overall, it is meaningful to briefly discuss the differences in the properties of this natural polymer as a function of the extraction procedure. Kraft lignin (KL) is the poly-dispersed, branched, phenol rich polymeric material obtained from the native lignin by the kraft (sulphate) pulping process. KL constitutes about 85% of the world's lignin production.<sup>25-26</sup> Due to the pulping process, the chemical structure of KL changes dramatically from the native one. It has higher amounts of phenolic –OHs due the breakage of the  $\beta$ -aryl bonds while condensed C-C bonds in it increase with the duration of pulping time.<sup>26</sup> Under certain conditions KL dissolves in water and its  $T_g$  varies between 124 – 174 °C.<sup>20, 27</sup> Lignosulfonates are obtained as a by-product from the sulphite pulping process.<sup>28</sup> These are mainly water-soluble polyelectrolytes containing large amounts of  $\text{HSO}_3^-$  and  $\text{SO}_3^{2-}$  anions. As such lignosulfonates are soluble in water and have a very broad molecular weight distribution (highest among the lignin obtained by the various pulping processes).<sup>26, 29</sup> Soda lignin is mainly obtained from the soda (a sulfur free technique) or soda-anthraquinone pulping process of annual plants like flax, straw and some of the hardwoods. Its  $T_g$  varies between 150 to 155 °C.<sup>30</sup> As such soda lignin is closer to the native lignin with respect to its chemical composition compared to KL or lignosulphonates.<sup>26, 31-32</sup> Organosolv lignin (OSL) is obtained by pulping processes that use organic solvents (ethanol, acetic acid, formic acid) and water.<sup>26, 33</sup> During this process, lignin is separated based on its solubility in a particular solvents. As OSL is obtained by a comparatively mild procedure, it is able to maintain higher homogeneity and chemical resemblance to the native lignin. These materials have lower molecular weight distributions, polydispersity, and lower solubility in water compared to the lignin obtained by other pulping processes.<sup>34-35</sup> OSLs are reported to have comparatively lower  $T_g$  ranging between 91 – 97 °C.<sup>20, 27</sup> During the steam explosion pulping method, lignin is separated from the cellulosic material by the application of steam under high pressure (16 – 34 kg/cm<sup>2</sup>) at a temperature range of 200-240 °C in a closed reactor.<sup>36</sup> "Steam-exploded lignins" generally show  $T_g$  in the range of 113 – 139 °C.<sup>20</sup> Corn stover lignin obtained during the cellulosic ethanol production is reported to have a high  $T_g$  of around 200 °C.<sup>37</sup>

**Thermal properties of lignin:**

Lignin is moderately stable at elevated temperatures due to its highly aromatic backbone. Previous reports show that upon heating during thermogravimetric analysis (TGA) under a nitrogen atmosphere, KL suffers a major mass loss (about 40%) between 200 to 600 °C. The maximum mass loss is observed around 400 °C.<sup>38</sup> It is reported that about 15% of the mass loss is observed below 300 °C. Fenner and Lephardt reported that the weight loss of softwood kraft lignin (SKL) between 150 to

300 °C is attributed to the elimination of formic acid, formaldehyde, carbon dioxide, sulfur dioxide, and water resulting from the degradation of the phenylpropane side chains at elevated temperatures.<sup>39</sup> However, it is also observed that upon an oxidative pre-treatment followed by heating around 200 – 300 °C for 30 to 60 min prior to the TGA analysis, the thermal stability of lignin improves substantially and the TGA traces then show less than 10% weight loss below 300 °C. This is attributed to the incorporation of oxygen in lignin in the form of carbonyl groups during heating in the presence of air. The incorporation of oxygen balances out the elimination of the volatile materials. As a result, no significant weight loss is observed below 300 °C.<sup>38, 40</sup>

Generally, lignin has a very interesting thermal behaviour and can act as a thermoplastic as well as a thermoset material. It behaves as a thermoplastic due to its chemical structure and intra- and inter-molecular hydrogen bonds<sup>41</sup> but occasionally lignin's poor flow properties prevent its use as a thermoplastic.<sup>42</sup> Therefore, to improve the flow property of this natural polymer it is often blended or copolymerized with other synthetic polymers so that the resultant material can be used as a thermoplastic material.<sup>41</sup> On the other hand, it has been found that at elevated temperatures, lignin forms cross-linked structures and behaves as a thermosetting material.<sup>41, 43-44</sup> Argyropoulos et al. have reported this behaviour and described that at elevated temperatures, SKL undergoes radical initiated self-polymerization leading to a dramatic increase in its molecular weight. They also showed that when SKL is heated 20 °C above its  $T_g$  (at 173 °C,  $T_g = 153^\circ\text{C}$ ) for 20 min, under nitrogen atmosphere, it shows a large increase in its molecular weight. Continuing heating for 30 min makes the material insoluble in common organic solvents (THF, DMSO, acetone) most likely due to the creation of three-dimensional cross-linked structures.<sup>43</sup>

Pucciariello et al. discussed that the DSC traces (obtained by heating from 60 °C to 200 °C at the rate of 20 °C/min) of lignin obtained from straw through steam explosion, showed a distinct endotherm around 161 °C on the first cycle of heating which was attributed to the  $T_g$  of the natural polymer by the authors.<sup>40</sup> However, on the second cycle of heating they did not find any endotherm up to 200 °C. The disappearance of the  $T_g$  in the second cycle is only possible if lignin undergoes self-polymerization and crosslinking during the first cycle of heating within the DSC instrument.

Although lignin has structural benefits, and natural abundance that makes it a well-deserved contender for commercial applications, its thermal instability confines its proper use. This is probably one of the reasons why only 2% of the lignin obtained from the pulp and paper industry is at present commercialized.<sup>19</sup>

In this article we aim to clarify how the incorporation of lignin in a synthetic polymer (in the form of copolymers, blends, and composites) modifies the thermal properties of the end

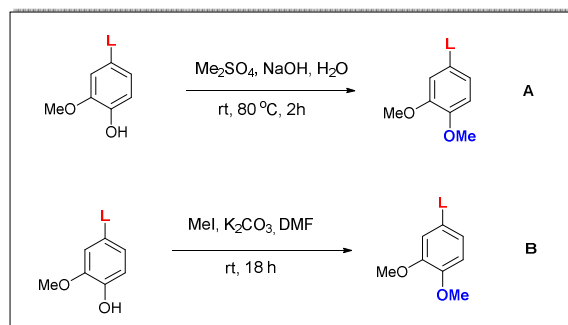
products. As shown in Fig. 2, lignin possess an aromatic rich polymeric structure having different types of functional groups especially the phenolic hydroxyl groups, which can further be exploited for lignin functionalization as well as for lignin chain extension to obtain higher molecular weights. Additionally, each year a large amount of lignin is generated as a by-product from the pulp and paper industry worldwide. The United State alone produces  $25 \times 10^6$  tons (imperial) of KL every year.<sup>45</sup> Due to its aromatic chemical structure and natural abundance, lignin offers tremendous commercial opportunities for modern day applications as an alternative source of aromatic polymeric precursors, polymers and energy. Moreover, lignin is biodegradable when in contact with various microorganisms<sup>12, 46-48</sup>. Consequently, either lignin itself or lignin-based polymers have the potential to be used as green alternatives to petrochemical based polymers. There are numerous reports available showing the use of lignin with other synthetic polymers for making blends, composites, or copolymers keeping its financial advantages in mind.

#### Thermal properties of lignin copolymers, blends and composites:

**Lignin copolymers:** One of the approaches to make value added compounds from lignin is its copolymerization with synthetic polymers.<sup>49</sup> As such it is worthwhile to discuss the effect of derivatization on the thermal properties of the polymer. This in general affects its  $T_g$  since it functions as an internal plasticizer.<sup>34</sup>

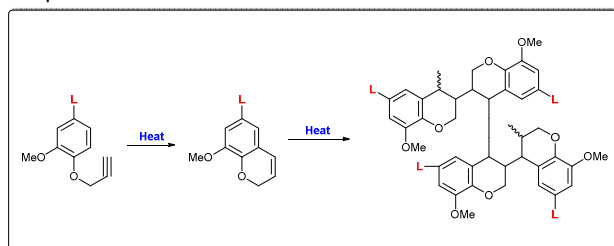
**Alkylation and alkoxylation:** Alkylated or alkoxyated lignins are comparatively easier to synthesize, purify, and characterize.<sup>34</sup> Due to the presence of a very large amount of phenolic hydroxyl groups especially within the structure of technical lignins i.e kraft etc., alkylation or alkoxylation can be effortlessly carried out stoichiometrically through nucleophilic aromatic substitution reactions ( $S_NAr$ ). As such these are well-acknowledged derivatization reactions to produce lignin ethers and hydroxyalkyl lignins respectively with the latter having the potential to be used as a pre-polymer for lignin based polyurethane synthesis reacting with diisocyanates.<sup>50</sup> However, like other polymers, these derivatizations work as an internal plasticization for lignin and its effect on the  $T_g$  of the natural polymer is very evident.

The major part of the alkylated lignin is used to prepare polymer blends mixing with synthetic polymers which will be discussed in subsequent parts of this review. However, there are a few research efforts where the thermal properties of the natural polymer derivatives are studied by themselves which show that the methylation (Scheme 1) reduces the  $T_g$  of the SKL as anticipated. The  $T_g$  of an unsubstituted SKL (153 °C) reduces to 128 °C upon complete methylation since the intramolecular hydrogen bonds get eliminated after complete derivatization.<sup>43, 51</sup> Moreover, alkylation completely removes the possibility of radical initiated self-polymerization of the KL making it an important step for commercial processing of this natural polymer.<sup>43</sup>



Scheme 1: Methylation of lignin using A) dimethyl sulfate, and B) methyl iodide.<sup>42, 50</sup>

Recently, Sen et al. reported a green method for KL methylation using benign dimethyl carbonate. This study also shows reduction of the  $T_g$  of the KL as a function of lignin methylation. It is worth mentioning here that the authors reported the methylation of both aliphatic and aromatic hydroxyl groups.<sup>52</sup> Similarly, the method of propargylation of hydroxyl groups in lignin introduces additional unsaturated moieties in the polymer structure which can further react with each other upon heating leading to a cyclized product. The decomposition temperature (measured by TGA) of the propargylated lignin increases significantly compared to the underivatized polymer and it increases further with the increase in the degree of propargylation.<sup>53</sup> The DSC traces of the propargylated SKL showed a large exotherm between 140 – 250 °C, which was attributed to a Claisen rearrangement reaction followed by thermal polymerization of the propargyl aryl ether moiety of the propargylated lignin samples as shown in Scheme 2. Hence the improvement in the thermal stability observed in the TGA experiment is also due to the formation of chain extended polymers obtained at elevated temperatures.<sup>53</sup>

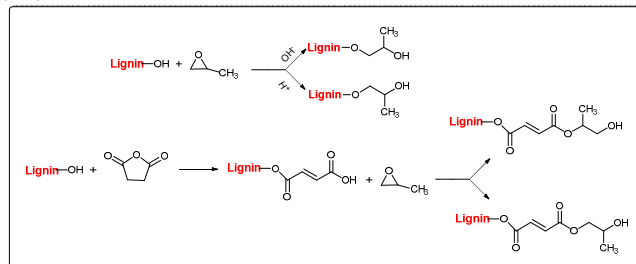


Scheme 2. Claisen rearrangement reaction followed by thermal polymerization of propargylated softwood kraft lignin.<sup>52</sup>

Several years ago, Kelly and co-workers synthesized hydroxypropyl lignin and chain extended hydroxypropyl lignin reacting both OSL and KL with one equivalent and excess propylene oxide respectively. These pre-polymers were further used for the synthesis of lignin-based polyurethanes.<sup>54-57</sup> However, before crosslinking with amines, the authors investigated the thermal properties of the chain extended lignin. They determined the  $T_g$  of the copolymers by heating them between -80 °C to 120 °C and observed that irrespective of the type of lignin used, the  $T_g$ s of the copolymer decreased with increase in the polypropylene content.<sup>55-56</sup> The reduction in the  $T_g$  is also in agreement with  $T_g$ s theoretically calculated

by the Gordon-Taylor equation (Eq. 1, B).<sup>58</sup> Comparatively, simple structured propylene oxide segments seem to offer flexibility in the complex lignin structure by increasing its segmental mobility. This can also be observed in the reduction of the  $T_g$  of the copolymer. Furthermore, the large amounts of phenolic hydroxyl groups present in pure lignin, contribute towards its higher  $T_g$  through the formation of intra-molecular hydrogen bonds and thereby creating a physically cross-linked structure.

However, after the alkoxylation reaction, the phenolic hydroxyl groups were converted to less acidic secondary aliphatic hydroxyl groups, which eventually reduced the extent of intra-molecular hydrogen bonding and thereby reduced the  $T_g$ . The efforts on the synthesis of wheat straw soda lignin based hydroxypropylated lignin were reported by Ahvazi and coworkers.<sup>59</sup> In this study, the authors reported two different approaches to synthesize lignin-based polyols (Scheme 3). In the first method, they studied reactions of lignin with maleic anhydride (1:10 mol ratio) to synthesize the corresponding polyesters. In these reactions almost 67% of the hydroxyl groups of the lignin (including the aliphatic and phenolic) were reported to have reacted with maleic anhydride as confirmed using quantitative  $^{31}\text{P}$  NMR spectroscopy.<sup>59</sup> As anticipated the amount of carboxyl groups was reported to increase after the esterification reaction. These prepolymers were further reacted with propylene oxide to synthesize the corresponding polyols as shown in Scheme 3.

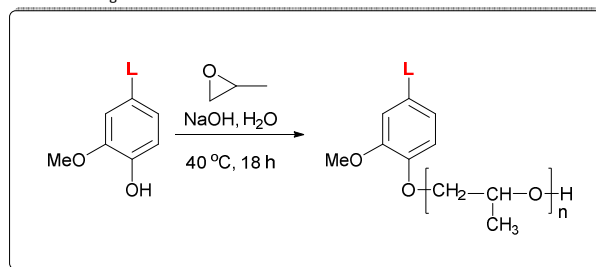


Scheme 3. Hydroxypropylated lignin synthesis reported by Ahvazi.<sup>55</sup>

Typically 46% of the total hydroxyl groups were seen to remain unreacted after reaction with propylene oxide. The initial esterification was shown to improve the compatibility of the lignin with the polyols. The  $T_g$  of the starting lignin (104.39 °C) was reported to reduce after reacting it with maleic anhydride (89.22 °C) mostly because of the destruction of intra- and inter-molecular hydrogen bonds. This was seen to further decrease upon reaction with propylene oxide making the  $T_g$  of the end product as low as 59 °C. Although the reaction with propylene oxide introduced new secondary aliphatic -OHs in the copolymer capable of forming hydrogen bonds, their strength was much lower than the initial phenolic -OHs (as phenolic -OHs are more acidic than aliphatic -OHs). Moreover, the introduction of alkyl chains increased the segmental mobility of the polymer, which was reflected in further reduction of the  $T_g$ . During an alternative approach, lignin was directly treated with propylene oxide separately in basic and acidic media to synthesize polyols.<sup>59</sup> The authors have shown

that the direct hydroxypropylation was more effective in alkaline medium since the reduction in phenolic hydroxyl groups and the concomitant increase in aliphatic hydroxyl groups were higher as seen by quantitative  $^{31}\text{P}$  NMR analyses. However, the  $T_g$  and thermal processibility of these materials were not discussed in detail.

Selective hydroxypropylation of the phenolic hydroxyl groups of SKL (almost 100% selective) can be done using propylene oxide in a basic medium (Scheme 4),<sup>51</sup> while the aliphatic hydroxyl groups remains unreacted. (The quantification of the phenolic -OH group disappearance and aliphatic -OH groups introduction was done by well established  $^{31}\text{P}$  NMR spectroscopy.)<sup>60-61</sup> Despite the fact that new aliphatic hydroxyl groups are introduced after the derivatization (as revealed from  $^{31}\text{P}$  NMR spectroscopy) the  $T_g$  of the hydroxypropylated lignin (128 °C) reduces significantly, compared to the starting material ( $T_g$  153°C).<sup>43</sup>



Scheme 4. Hydroxypropylation of lignin.<sup>50</sup>

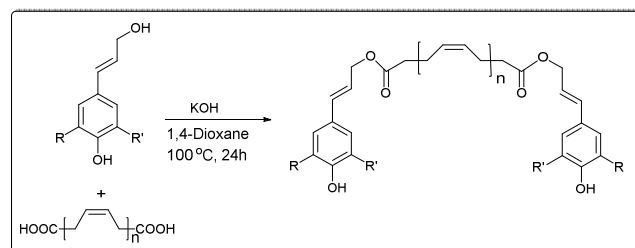
This brings us to the conclusion that upon alkylation the intra-molecular hydrogen bonds of lignin are destroyed. Whereas, upon alkoxylation the more acidic phenolic -OHs are replaced by comparatively less acidic secondary aliphatic -OHs which does not have the potential to create strong intra-molecular hydrogen bonds. Besides, the introduction of the alkyl chain promotes the segmental mobility of the copolymer. Overall, both alkylation and alkoxylation result in the reduction in the  $T_g$  of a derivatized lignin.

**Esterification:** Polyesters are well known synthetic polymers widely used in the textile and packaging industries. Especially polyesters having combined aliphatic aromatic structures (for example polyethylene terephthalate) provide unique thermal properties. While polyethylene terephthalate has a comparatively lower  $T_g$ , (67 °C) it has a high melting temperature (265 °C).<sup>62</sup> Both the monomers of polyester (diol and dicarboxylic acid) are obtained from either petroleum or natural gas resources. As such efforts to substitute either one or both the monomers with lignin or lignin derivatives to make the process greener need to be reviewed here. The diol has been substituted with KL for thermoplastic polyester synthesis using sebacoyl chloride as the other monomer.<sup>63</sup> In this study, the  $T_g$  of the copolymer measured using complex electric modulus (CEM) procedures, showed that the lignin based polyesters had a  $T_g$  around 70 °C irrespective of the reaction temperature or the co-monomer ratio used. The thermal stability (measured using TGA) of synthesized copolymers

increased with increasing reaction temperature, and concentration of sebacoyl chloride in the reaction mixture. Increasing the reaction temperature or concentration of sebacoyl chloride also increased the molecular weight of the polymer. Therefore, the improved thermal stability of the lignin-based polyesters can be accredited to the higher molecular weight of the resultant polymer. The polymer degradation was found to start between 180 – 210 °C which made it feasible to process the polymer around 140 °C without producing odour and/or fumes.<sup>63</sup>

Fox and McDonald reported the synthesis of lignin-based polystyrenes reacting three different types of lignins (SKL, corn stover and rice straw lignin) with acetic, propionic and butyric anhydrides respectively. The DSC thermograms of the resultant bio-based polyesters showed that irrespective of the lignin used, lignin acetate always has a highest  $T_g$  while lignin butyrate has the lowest  $T_g$ .<sup>64</sup>

Later, Saito et al. described their work regarding hardwood kraft lignin (HKL) based thermoplastic polyester synthesis copolymerized with carboxy terminated telechelic polybutadiene (PBD(COOH)<sub>2</sub>).<sup>65</sup> In this effort, the authors selected to work with the methanol insoluble fraction of lignin after partially crosslinking it with formaldehyde (F-lignin) to get a higher molecular weight and glassy sample.<sup>66-68</sup> The  $T_g$  of the above-mentioned lignin derivative was found to be higher than its degradation temperature ( $\approx$  220 °C) and therefore, could not be determined. The polyester products (F-lignin-PBD(COOH)<sub>2</sub>) were synthesized reacting varying amounts of F-Lignin (12, 22, 30, 38 wt-%) with (PBD(COOH)<sub>2</sub>) as shown in Scheme 5.



Scheme 5. Polyesters synthesized by Saito et al.<sup>58</sup>

All samples could form freestanding thermoplastic films at room temperature. The DMA studies of the films formed from F-lignin-PBD(COOH)<sub>2</sub> copolymers showed the presence of two phases and viscoelastic behaviour.<sup>65</sup> In these copolymers, the lignin part constituted the hard segment while the PBD(COOH)<sub>2</sub> part constituted the soft one. Thus, it is reasonable to conclude that the first transition obtained from glassy to rubbery phase was the  $T_g$  of the PBD(COOH)<sub>2</sub> segment. In addition the  $T_g$  did not change that much with an increase in the amount of F-lignin in the copolymer when measured through both  $E''$  and  $\tan\delta$  procedures. The  $T_g$  obtained from the DSC thermogram was found to vary between – 81 °C to -78 °C supporting the data obtained from the DMA studies. A second transition in  $E''$  was observed

between 8 °C to 24 °C.<sup>65</sup> This was attributed to the softening temperature of the lignin segment. However, no second  $T_g$  was observed in the DSC thermogram of the copolymer, neither the  $T_g$  of the pure F-lignin. The flow property of the copolymer improved remarkably compared to the starting F-lignin. This was most likely due to some plasticization effects in the copolymer, which in turn improved the flow property of the copolymer.

Highly branched poly(ester-amines) can be synthesized from lignin precursors. In a relevant study, the monomer precursors were first synthesized by reacting 1,1,1-triethanol amine with different dicarboxylic acids to yield highly branched poly(ester-amine)s (HBPEA) followed by reacting the ester-amine)s with lignin offering lignin based branched poly(ester-amine)s (L-HBPEA) as shown in Scheme 6.<sup>69</sup> These bio-based materials were flexible at ambient temperatures but insoluble in common organic solvents because of their three-dimensional structure. Similar to other hyperbranched materials, L-HBPEA samples also displayed low viscosities. These copolymers offered a single  $T_g$  confirming the presence of a single phase. For a particular dicarboxylic acid, the  $T_g$  was seen to increase with increasing content of lignin in the sample. With increase in the amount of lignin, the extent of phenolic hydroxyl group increased which eventually increased the crosslinking density in the polymer. Additionally, the remaining free phenolic hydroxyl group participated in inter-molecular hydrogen bonding increasing the  $T_g$  of the material.

This result also confirmed that the presences of inter- and intra-molecular hydrogen bonds were mainly responsible for the improved  $T_g$  of the materials at higher lignin contents. It was also shown that the  $T_g$  of the copolymer decreased with an increase in the chain length of the dicarboxylic acid. This was anticipated since increasing the chain length reduced the crosslinking density and thus increased the molecular mobility in the copolymer. The  $T_g$ s of the hyperbranched copolymers were found to be affected more with the amount of the lignin content in the copolymer than the straight chain copolymers. In case of straight chain copolymers, the molecular weight increases with the increase of lignin content which does not have any profound effect on the  $T_g$ . In case of hyperbranched copolymer, increase in the lignin content opens up the possibility of more hydrogen bonds (if possible) and as such the whole structure grows in size. Therefore an increase in the glass transition temperature is reasonable.

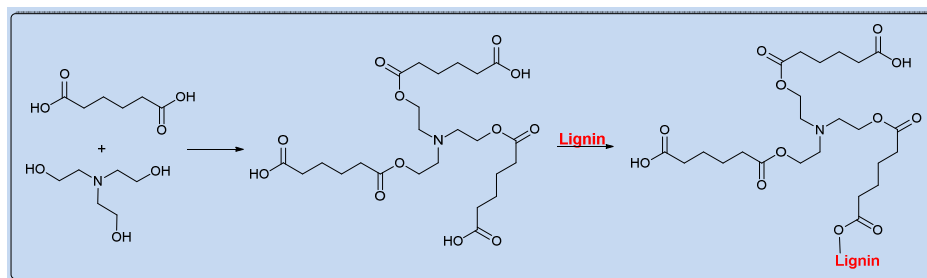
In a recent study synthesis of hyper-branched lignin copolymers has been described in great detail. In this effort macromonomers were synthesized using glycerol, adipic acid, and diisopropanolamine or tris(hydroxymethyl) aminomethane. Then these macromonomers were treated with soda lignin to get the desired hyper-branched product. All copolymers showed a single  $T_g$  confirming the presence of a single phase and great miscibility between lignin and the



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premonomer. It was also found that the  $T_g$  increases with increasing amount of tris(hydroxymethyl) aminomethane. The TGA thermograms of the copolymers reveal that the copolymers have three stage decomposition. The first two states (200-400 °C and 400-440 °C) are due to thermal degradation of the macromonomer while the third thermal decomposition (440-549 °C) is strictly for the lignin segment.<sup>70</sup>



Scheme 6. Lignin based highly branched poly(ester-amine)s synthesized by Sivasankarapillai and McDonald.<sup>69</sup>

KL can also be reacted with  $\epsilon$ -caprolactone (CL) to obtain a chain extended lignin-based caprolactone pre-monomer, which can be further used to synthesize bio-based polyesters.<sup>42</sup> During this reaction, an excess of CL was used to make sure all the easily available hydroxyl groups of lignin were capped by CL, leaving behind the most sterically intricate and hard to reach hydroxyl groups. Special care was taken to minimize the crosslinking formation in the subsequent polymer by end capping only two hydroxyl groups of each lignin chain as much as possible. The pre-monomers were further reacted with sebacoyl chloride to obtain the desired polyesters.<sup>42</sup> Due to the lower reactivity of the remaining hydroxyl groups of the KL, compared to those of the CL unit (steric hindrance considerations), sebacoyl chloride selectively reacted with the hydroxyl groups of the CL units imparting a linear structure to the polymer. The resultant polyesters showed dramatically improved thermal stability compared to the parent lignin. 2% weight loss of the pure lignin took place around 80 °C while the copolymer required around 200 °C for the same weight loss. As the copolymerization conveyed linearity, the flow property of the polymers was also improved significantly. The viscosity of the subsequent lignin based polyester decreased when the temperature is increased and transformed into a liquid around 200 °C. However, pure KL did not show any signs of liquefaction upon heating. It remained a dark brown powder. FT-IR studies of the heat-treated pure lignin confirmed the formation of intermolecular and intramolecular crosslinking in the material. When free hydroxyl groups of the lignin samples were masked during the caprolactone derivatization, the material was observed to be more stable at elevated temperatures. As such this study

definitely indicated that the derivatization of lignin with caprolactone improved its thermal stability and flow characteristics, crucial factors for the material's thermoplastic potential.

TGA analyses of the OSL based polyesters showed their thermal stability to increase up to 300-325 °C, with the maximum rate of volatilization occurring at around 430-450 °C. The percentages of graphitized residues were lower than those obtained from solution polyesters, but naturally increased with increasing lignin content.<sup>71</sup> Polyesters obtained from the reactions of SKL with dicarboxylic aliphatic (sebacoyl) or aromatic (terephthaloyl) acid chlorides showed very interesting thermal behaviour. The lack of melting points in the DSC traces confirmed the amorphous nature of the copolymers. In the study it was also found that the thermal stability improved compare to the starting KL.<sup>72</sup> At this point it is important to note that the above discussion elucidated that lignin has been successfully used as a substitute for diols in polyester synthesis. Lignin based polyesters have unique thermal properties. The thermal stability of the copolymers seems to improve compared to the starting lignin material while the  $T_g$  widely depends on the diacids used.

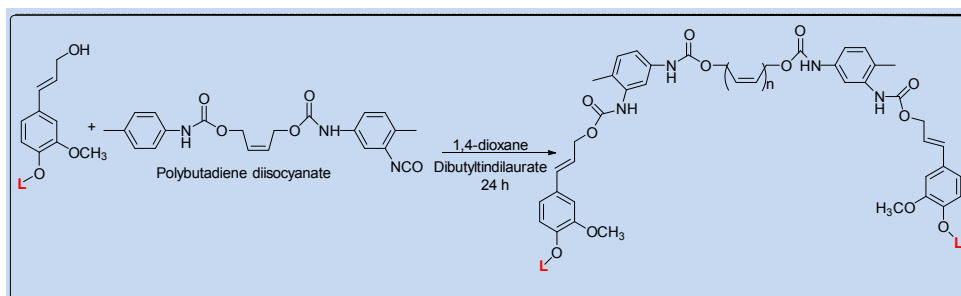
**Polyurethane Synthesis:** Being an aromatic rich polymer, lignin is a tough material with comparatively high  $T_g$ s. As such it is reasonable to synthesize block copolymers reacting it with a soft elastomeric material to form thermoplastic elastomers where the hard lignin segment provides mechanical strength to the





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Scheme 7. Lignin based polyurethane synthesized by Saito et al.<sup>73</sup>

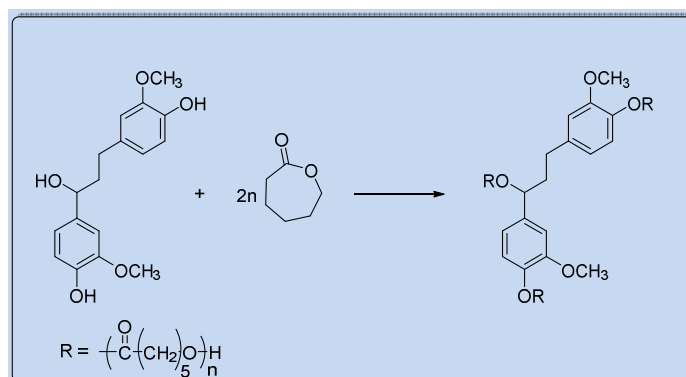
polymer and the soft synthetic polymer delivers rubbery flow characteristics. These types of lignin based thermoplastic elastomers can be used as a replacement for vulcanized rubber, adhesives, coatings, sealants, polymer blends and modifiers of thermosetting materials.<sup>65, 74</sup>

Lignin polyurethane copolymers are good examples of thermoplastic elastomers. Since lignin is a hard material, it provides mechanical strength to the copolymer while the soft polyurethane helps the flow characteristics of the material.<sup>73, 75</sup> In this context Cheradame et al. reported their studies regarding the synthesis of polyurethanes using SKL and hexamethylene diisocyanate.<sup>76</sup> The authors have reported that the thermal stability of the polymer improved with increasing lignin content, which can be attributed to the fact that the lignin contents added more highly aromatic structure to the resulting polymer. Also, the  $T_g$  increased with the increase in lignin content beyond 18-wt%. The hard segment lignin was anticipated to offer restrictions to the segmental motion of the polymer through its rigid aromatic structure. Therefore, the increase in the  $T_g$  was not surprising.

Thermal properties of lignin-based copolymers are highly dependent on the chemical structure of the lignin used for the copolymer synthesis. The  $T_g$  of the partially crosslinked elastomer synthesized by reacting OSL and oligo ethylene oxide di-isocyanate decreased with a decrease in the fraction of lignin in the polymer.<sup>71</sup> This result was quite expected as lignin provided the harder segment in the copolymer (due to its rigid aromatic structure). The dependence of the  $T_g$  on the solvent used to extract the lignin from the lignocellulosic material had also been reported. For example, polyurethanes synthesized with acetic acid extracted hardwood lignin showed a higher  $T_g$  (-38 °C) than that of polyurethanes synthesized from ethanol (-44 °C) or acetone (-44 °C) extracted lignin. Acetic acid was found to extract the lignin fraction with a

lower amount of hydroxyl group (0.80 per C9 unit) present in it compared to the lignin extracted with methanol (1.18 per C9 unit) or acetone (1.23 per C9 unit).<sup>71</sup> Higher amounts of hydroxyl group per structural unit of lignin extracted with ethanol and/or acetone were seen to react with higher amounts of di-isocyanate. As such due to the increase in soft segment in the copolymer, the  $T_g$  was further reduced.

In another effort Saito and co-workers depicted the copolymerization of lignin and isocyanate to form lignin based thermoplastics polyurethanes (Scheme 7).<sup>77</sup> In this effort, the authors used the methanol insoluble fraction of hardwood OSL partially cross-linked with formaldehyde (F-lignin) similar to their earlier work regarding lignin based polyester synthesis.<sup>65</sup> A mildly cross-linked F-lignin with  $T_g$  of 154 °C (not the highly cross-linked F-lignin synthesized by the authors where  $T_g$  was higher than the degradation temperature of lignin) was used for the polyurethane synthesis since the former would be suitable for the preparation of melt processable thermoplastic copolymers.<sup>65</sup> The authors synthesized a series of four copolymers (F-lignin-OCN-PBD-NCO) by reacting different ratios of F-lignin (65, 70, 75 and 80 weight-%) (hardwood OSL) with polybutadiene diisocyanate.<sup>77</sup> Films were then casted from the copolymer solution and subjected to DMA and DSC tests. Both DMA and DSC data indicated the presence of two  $T_g$ s for the copolymers; irrespective of the amount of F-lignin present in it. This certainly verified the ideal two-phase (glassy and rubbery) morphology of the copolymer. The first  $T_g$  was found to occur at around -32 °C to -34 °C which was attributed to the transition of the rubbery OCN-PBD-NCO phase (the  $T_g$  of pure OCN-PBD-NCO is -35 °C). The second  $T_g$  was found to occur at around 150 °C which was attributed to the transition of the F-lignin segment (the  $T_g$  of pure F-lignin is 154 °C).<sup>77</sup> This data



Scheme 8. Lignin based chain extended polyurethane synthesis reported by Hatakeyama et al.<sup>78</sup>

indicated that minor variations in the monomer ratio did not change the thermal behaviour of the soft and hard segments drastically.

Similarly, Hatakeyama et al. reported their studies regarding lignin-based polyurethane synthesis via chain extension through the reaction with caprolactone (Scheme 8).<sup>78</sup> In these studies, the authors first synthesized the lignin-based polycaprolactone (PCL) by reacting  $\epsilon$ -caprolactone (CL) with lignin (OSL extracted with alcohol and SKL). To vary the PCL chain length the authors used different molar equivalents (e.g., 1, 2, 3, 4, 5, 10, 15, 25) of CL per mole of total hydroxyl groups present in the lignin sample and found that both the aliphatic and phenolic hydroxyl groups were being substituted as shown in Scheme 8. The resulting lignin CL copolymers were further reacted with diphenylmethane diisocyanate to produce the terpolymer. All SKL derivatives were found to be thermally stable up to 350 °C. The  $T_g$  of the pristine KL used for the synthesis of the copolymer was found to be at 100 °C. However, the SKL polycaprolactone copolymers (KLCL) showed reduction in their  $T_g$ 's with increasing chain length of the PCL unit. The decrease in the  $T_g$  was expected as the intermolecular hydrogen bonding was disrupted as a result of the derivatization. Moreover, increasing the chain length of the polycaprolactone side chain was found to increase the segmental mobility of the copolymer showing an additional decrease in the  $T_g$  with increasing PCL content. Interestingly, the  $T_g$  was found to level off for the copolymers synthesized using more than 10 equivalents of CL per equivalent of hydroxyl group present in lignin.<sup>78</sup> With increasing caprolactone chain length the crystallinity grew in the PCL side chain. Furthermore the generation of an endothermic peak (attributed as the melting of PCL side chain) in the DSC trace of the polymer around 50 °C when more than 5 equivalent of PCL

was added confirmed the invoked crystallinity. As such growing crystallinity in the side chain controlled the molecular mobility of the whole copolymer restricting it from further mobility increases. This eventually translated to a levelling of the  $T_g$ . However, the terpolymer synthesized by reacting lignin based polycaprolactones with diphenylmethane diisocyanate showed no significant changes in the  $T_g$ .<sup>78</sup>

The thermal stability of the terpolymer lignin-2,5-toluene diisocyanate-hydroxy terminated polybutadiene (Lignin-TDI-HTPB) is better than the copolymer 2,5-toluene diisocyanate-hydroxy terminated polybutadiene (TDI-HTPB) and the decomposition temperature increases with an increase in the lignin content.<sup>75, 79</sup> The DSC traces of the samples also show that a greater amount of heat is required to degrade Lignin-TDI-HTPB compared to TDI-HTPB.<sup>79</sup>

Duong et al. reported the polymerization of lignin macromonomers and methylene diphenyl diisocyanate towards thermoplastic materials.<sup>80</sup> The resulting lignin-urethane polymers were obtained at 80 °C for 3-4 h and reached the highest molecular weight (up to 912,000 g/mol) reported so far for such type of polymerizations. The thermal stability of the resulting polymer was greatly increased resulting in the first degradation temperature ( $T_{2\%}$ ) at 204 °C and  $T_{max}$  at 463 °C, attributed to the fact that OH groups in lignin were replaced by urethane bonds.<sup>80</sup>

Like any other polyurethanes the thermal properties of lignin-based polyurethanes strongly depend on the chain length of the hard and soft segments. In their paper, Laurichesse et al. discussed the synthesis of lignin based polyols reacting OSL with fatty acid chlorides (oleic acid) which were further reacted with isocyanate pre-polymers (synthesized from Poly(propylene glycol) and 4,4'-methylene diphenyl

diisocyanate) to obtain polyurethanes. The molar ratio of NCO:OH was varied between 0.2 to 1.0.<sup>81</sup> In the above-mentioned lignin based polyurethanes (LPUs) lignin/oleic acid macro polyol (LOAP) constituted the hard segment while the isocyanate pre-polymer represented the soft segment respectively. Their relative compositions affected the thermal stability of the copolymer. The thermal decomposition of polyurethanes was a multistep process e.g. the decomposition of urethane bonds and the degradation of the soft segments.<sup>82</sup> As such the lignin based PU materials showed similar two-step decomposition behaviour. The first degradation step occurred between 200 °C and 300 °C and suggested that the decomposition of the hard segments, attributed to the LOAP component, while the second step was attributed to soft segment decomposition between 350 and 400 °C. These LPU's showed the best thermal resistance, which might be due to the high content of LOAP in the LPU matrix (from 89 to 63% w/w). The DSC and DMTA studies of these lignin based polyurethanes showed the presence of two phases as anticipated. The soft segment showed comparatively low transition temperature between (-48 °C to -10 °C) increasing with increasing chain length of the polyisocyanate pre-polymer while the hard segment showed comparatively high  $T_g$  (around 30 °C to 54 °C) concomitantly increasing with increasing crosslinking density.

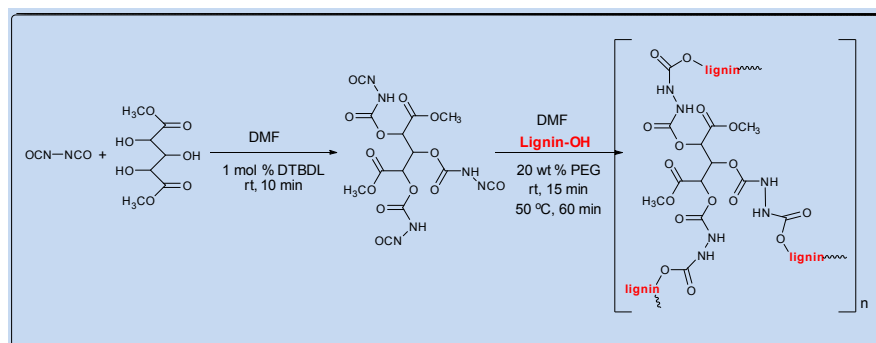
Similarly, lignin based thermosetting polymers synthesized via the condensation of lignin with hexamethylene diisocyanate (HDI) or of a mixture of lignin-poly(ethylene oxide) (PEO) with HDI has been reported.<sup>83</sup> Thermogravimetric analyses of these materials showed three main decomposition phases around 225, 340, and 465°C respectively. This thermal decomposition behaviour is quite different from that observed for lignin itself.<sup>83</sup>

Saraf et al. also reported the structure-activity relationship of lignin/PEG based polyurethane networks. They synthesized lignin based thermoset PU's using isocyanates; hexamethylene diisocyanate (HDI) and toluene diisocyanate (TDI) by solution casting.<sup>57</sup> According to their investigation, the  $T_g$  of the polyurethanes referred to the transition of the lignin phase since the transitions originating from the PEG component were not detectable. In this work the  $T_g$  was found to change significantly only with PEG content but the PEG molecular weight showed a less pronounced effect. Since the weight ratio of lignin polyol to the isocyanate component was kept constant throughout the series, the authors commented that that the NCO/OH ratio and the crosslink density varied at a constant lignin to PEG ratio and varying PEG molecular weight. Thus, incorporating more PEG makes the molecule more flexible increasing its molecular mobility as such it affects the  $T_g$ . However, increasing the molecular weight of PEG simply increase the molecular weight of the copolymer which does not have any effect on the  $T_g$ .

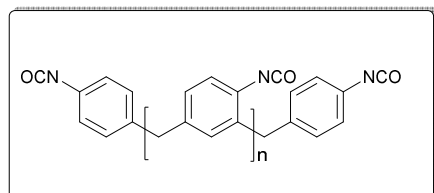
The initial increase in the  $T_g$  of the Mn 4000 sample prepared at < 5% PEG content may not be significant or may be due to increased crosslink density (NCO/OH ratio). The data of the HDI- and TDI-based films showed similar trends although at different temperature levels. TDI derived films generally displayed their  $T_g$ s at around 50°C above those of their HDI counterparts because of the aromatic structure of the diisocyanate. In short, the polyurethanes showed a steady drop in the  $T_g$  with increasing PEG content (more segmental motion) and a less dramatic increase with increasing molecular weights.<sup>57</sup>

Similarly, hydroxypropyl SKL-based thermosetting polyurethanes consisting of polybutadiene (PBD) glycol soft segments were synthesized using excess of hexamethylene diisocyanate (HDI) and tolylene diisocyanate (TDI). Solution casting techniques offered films containing glycol-based polyurethanes. The absence of a continuous drop in  $T_g$  with rising soft segment content was opposite to the results obtained with PE glycol soft segments, which displayed a constant decline in  $T_g$  with rising glycol content. The limitation of the  $T_g$ -reducing effect of PBD glycol to very low levels of polyol mixing could be explained by the poor solubility of PBD in the lignin derivative network (i.e., < 3.6% and < 7.1% for HDI and TDI-based polyurethanes, respectively). It was also interesting to compare the rubber-polyurethane films with the unmixed polyurethanes. A dramatic similarity between both was revealed with the rubber-networks showing transitions at a lower temperature with a steady decrease in  $T_g$  as a result of soft segment incorporation. This likely suggested that the modification of the lignin phase (via plasticization) was due to the reactions of the glycol with the lignin. However, it was observed that the increase in NCO/OH ratio in the unmixed films originated from higher proportions of diisocyanate, whereas in the case of mixed films, it originated from the chemical differences of the OH functionalities as well as stoichiometry considerations. The increase in the lignin  $T_g$  of TDI-based films was due to differences in hard segment crosslink density with varying glycol contents. Since the PBD glycol used had a much lower hydroxyl content (0.83 meq/g) than the hydroxypropyl lignin (2.52 meq/g), the replacement of lignin with PBD glycol lowered the isocyanate requirement of the polyol component and increased considerably the crosslink density at constant isocyanate content. The comparative insensitivity of  $T_g$  towards crosslink density (NCO/OH ratio) variations of the HDI-based films matches the behaviour of soft segment-free lignin polyurethanes.<sup>57</sup>

Oxypropylation of lignins and preparation of rigid PU foams from the ensuing polyols is another method that improves the thermal characteristics and properties of lignin.<sup>84</sup> Oxypropylation of OSL and soda lignin turned out to be the most direct process for such conversions. The ensuing polyols (glycerol) are viscous products with functional

Scheme 9: Synthesis of prepolymer and lignin polyurethanes.<sup>85</sup>

characteristics very similar to those of conventional compounds used in the preparation of polyurethanes (PMDI, methylene diphenyl diisocyanate) (Fig. 3). Moreover, the rigid polymeric polyurethane foams (RPU) obtained from the combination of polyols (glycerol) and polyisocyanate (MDI, with NCO functionality) showed good thermal properties and dimensional stability, even after ageing.<sup>84</sup>

Figure 3: Chemical structure for polymeric methylene diphenyl diisocyanate.<sup>79</sup>

The thermal properties of SKL-based polyurethane films synthesized by solution casting from hydroxypropyl lignin derivatives and either an aliphatic or an aromatic isocyanate were investigated by Saraf et al.<sup>57</sup> These authors selected two types of lignins; kraft and steam explosion lignin, and two diisocyanates, HDI and TDI, for their work. DSC thermograms of the polyurethane films showed that the  $T_g$ s of thin films were generally below those of the corresponding lignins. A gradual increase in the  $T_g$  was seen with increasing NCO/OH ratios. Between the two isocyanates selected, TDI based films had  $T_g$ 's higher than those of the corresponding HDI films at the same NCO/OH ratio (because of the aromatic structure).<sup>57</sup> It was also observed that the  $T_g$  of TDI-based films increased more steeply with the NCO/OH ratio than the  $T_g$  of their HDI equivalents. At very high isocyanate concentrations, the  $T_g$  of both films began to level off or decrease. While it was likely that the crosslink density could still be increasing, the possible reason for this decrease is that the segmental contribution by HDI through the hexamethylene "soft segments" had an overriding influence on the thermal properties.<sup>57</sup> Pohjanlehto

et al. reported of polyurethanes synthesized from SKL via the synthesis of a pre-polymer created from the esterified sugar-based trihydroxyl compound xylaric acid, followed by an excess of MDI (Scheme 9).<sup>85</sup> The pre-polymer was crosslinked with 5, 10, and 15 wt % of an industrial soda lignin, and polyethylene glycol (PEG) was used to incorporate soft segments into the material. The thermal properties of the materials were tested by DSC and TGA. The  $T_g$  obtained from DSC and DMA studies showed a trend of increasing  $T_g$  with increasing amounts of lignin (hard segment). A similar trend was observed in their TGA work i.e increasing thermal stabilities up to 550 °C with increasing amounts of lignin.<sup>85</sup>

Similarly, Misra et al. reported that the lignin/soy-based polyurethane bio-foams showed improvements in thermal properties,<sup>86</sup> suggesting interactions like covalent and hydrogen bonding between lignin and the bio-polyurethane. Lignin seemed to function like a chain extender and cross-linking agent for the bio-polyurethane moieties. The effect of the amount of lignin on the thermal stability of these Bio polyurethane composites was significant and was evaluated by TGA under a nitrogen atmosphere.<sup>86</sup> The first downturn was observed above 200 °C. The derivative TGA curve corresponding to neat polyurethane revealed four peak maxima suggesting at least four main degradation processes. The same trends were also observed with 5, 10 and 15-wt% of lignin of the same decomposition pattern. The decomposition of urethane bonds started around 200 °C.<sup>87</sup> These data suggested that softwood lignin did not affect the basic mechanisms of the thermal degradation of the bio-based polyurethane but improved its thermal stability.

Additionally, Nakamura et al. investigated the thermal behaviour of solvent-cast PU films derived from the solvolysis of softwood lignin (SL) obtained as a side product of a pulping process.<sup>88</sup> Their studies suggested that the thermal properties

of the solvolysis lignin-PEGMDI (PEG, diphenylmethane diisocyanate) derived polyurethanes could be controlled by changing the solvolysis lignin and PEG contents at a certain NCO/OH ratio. Moreover, the results from these studies showed that the  $T_g$  of PU derived from SL was controlled mainly by the SL content. The rigidity of the phenyl groups in the main chain of SL is a major factor determining the  $T_g$  of PU, although the cross linking density and the molecular length of the soft segment in PU affected  $T_g$  values to a small extent. The decomposition of the PU's was distinctly dependent on the content of SL in the PU's. The other factors, such as the NCO/OH ratio and the Molecular weight value of PEG, were less controlling factors than the amount of SL. The authors invoked an undefined dissociation between the isocyanate groups and the phenolic hydroxy groups in SL as being the major factor in the process of the thermal decomposition of the PU containing SL.<sup>88</sup>

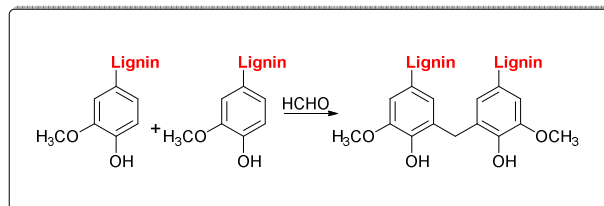
Polyurethane (PU) films were also prepared by solution casting using a three-component system consisting of a low molecular weight fraction of SKL, PEG of various molecular weights, and crude MDI as starting reagents.<sup>89</sup> DSC studies showed that the PU films were cured to stable properties at 95°C (8 h). The samples were, however, somewhat unstable at higher temperatures, probably due to additional curing. The  $T_g$  was found to decrease at a given KL content, with increasing sequence length of the PEG chain. This can be attributed to the reduction in crosslink density discussed above and to the increase in PEG that followed with increasing molecular weight of PEG at a given KL content and NCO/OH ratio.<sup>89</sup>

Phase separation between the soft and hard segments is a well-recognized phenomenon in the case of linear, thermoplastic PU elastomers. The hard segments were considered to associate through urethane-urethane hydrogen bonds.<sup>89</sup> Accordingly, two different  $T_g$  can be observed in most cases. The thermal stability of the lignin-based polyurethanes generally improves compare to the commercially available polyurethane due to the aromatic rich structure of lignin.

#### Lignin based phenol formaldehyde resins:

Phenol-formaldehyde (PF) resins are well known synthetic polymers manufactured either in acidic or basic media and are widely used to prepare moulded products, coatings and adhesives. PF resins are well known for their chemical resistance, electrical insulation, excellent water resistance, chemical stability and dynamic stability.<sup>90-91</sup> Acid catalyzed PF resins known as Novolacs contains a phenol to formaldehyde molar ratio of more than one. Novolacs are generally thermoplastic materials<sup>92</sup> with the potential to form a cross-linked structure upon heating with a curing agent (hexamethylenetetramine). In contrast, base catalyzed PF resins known as Resols, usually contain phenol to formaldehyde molar ratios of less than one. With excess formaldehyde, Resols have the capability to form cross-linked three-dimensional structures by heating in the absence of a curing agent. Resols are thus known as thermoset resins.<sup>92</sup>

The growing price of phenol, however, highly restricts the production of PF resins. Due to the structural similarities between phenol and lignin, this natural polymer has tremendous potential to completely or partially substitute the role of the phenol in the synthesis of lignin based phenol formaldehyde resins. As such numerous efforts have been reported in this respect.<sup>92-100</sup>



Scheme 10. Lignin based PF resin synthesis.<sup>87</sup>

Lignin based PF resin synthesis is shown in Scheme 10, from which it is quite clear that to create lignin based PF resins at least one of the ortho positions of the phenolic hydroxyl group of the starting lignin must be unsubstituted so that this active site can participate in the reaction with formaldehyde. From our earlier discussions (Fig. 2), it is clear that H and G units (as these have at least one active site present) are able to react with formaldehyde to synthesize the lignin based PF resins while S (no active site is present) unit is not. Moreover, H units that possess more than one active site offer the potential to create highly crosslinked structures. Consequently lignins with G units would be ideal to create bio-based PF resins with a controlled structure. As such softwood lignin (containing mainly G units) are a better choice for lignin based PF resin synthesis than hardwood lignins (containing both G and S units).<sup>101</sup> Various reports have also shown that lignin derived from organic solvents are suitable to these types of bio-based PF resin synthesis due to their better solubility in phenol compared to native lignins.<sup>98, 102-103</sup> In this context Tejado and co-workers examined different types of lignin (pine KL, soda/AQ flax lignin and organosolve hardwood lignin) in order to determine the optimum conditions for the synthesis of lignin based phenol formaldehyde materials.<sup>25</sup> After in depth spectroscopic (FT-IR, NMR) and thermal studies, the authors concluded that the kraft pine (softwood) lignin would be the best choice for the synthesis of lignin based PF's since it has the maximum number of non-etherified free phenolic hydroxyl groups (kraft pine lignin is mainly composed of G units while AQ flax lignin and organosolv hardwood lignin are mainly made of S and S+G units respectively). Additionally pine KL has a higher molecular weight distribution compared to the other two lignin samples and its thermal stability is also analogous to that of the commercial novolac resins. The effort reported by El Mansouri and Salvado also supports Tejado's conclusions.<sup>104</sup> In their studies, El Mansouri and Salvado studied different sulfur containing (KL, lignosulfonates) and sulfurless (soda-antraquinone, organosolv and ethanol) lignin samples to find out an ideal material for lignin based phenol formaldehyde adhesive synthesis. After extensive studies the authors concluded that the KL was the best since it had the highest amount of phenolic hydroxyl groups (active sites) and the

lowest amount of methoxy groups allowing for optimal chemical reactivity. Additionally, the lower number average and weight average molecular weights of KL were also anticipated to aid the creation of bio-based phenol formaldehyde adhesives since it promoted its reactivity (based on steric hindrance considerations).

Later, Mansouri and his group reconfirmed that KL is ideal among different types of alkaline lignins (KL, soda-rice straw lignin, soda-wheat lignin). Amongst the examined lignins, kraft contained the lowest amounts of phenolic hydroxyl groups. Despite this, however, it showed highest thermal stability, a most suitable molecular weight range and a superior amount of G units. Overall the authors concluded that these considerations made SKL an ideal choice for the starting material for lignin based phenol formaldehyde resins.<sup>30</sup> Ibrahim and co-workers have also shown that between KL and soda lignin (both obtained from oil palm biomass) KL was a better starting material to create bio-based PF resins since it is of lower molecular weight, has higher thermal stability and lower  $T_g$  compared to other lignins.<sup>105</sup>

Later on, Perez et al. reported their studies to synthesize softwood ammonium lignosulfonate based lignin-phenol-formaldehyde materials.<sup>106-109</sup> In this study, the authors used softwood ammonium lignosulphonate directly as well as its methylol derivatives for the synthesis of such bio-based thermoset materials. They also compared the properties of the bio-based PF resins with the commercial phenol-formaldehyde.<sup>106</sup> Despite the fact that the structures of lignin based PFs were of considerable complexity (as studied by FT-IR and NMR spectroscopies) their physical properties (specifically softening point) were in the range of the commercial petrochemical based materials. However, the flow distances of the bio-based materials were found to be of a lower range than the range of the commercial synthetic materials. This was mainly attributed to the three dimensional structure of lignin, which restricted the flow of the resin. In another effort Perez and co-workers showed that the thermal stability of lignin (softwood ammonium lignosulfonate) based PF samples were much lower than the thermal stability of the commercially available counterpart.<sup>110</sup> This was mainly attributed to the lower thermal stability of the lignin sample itself at elevated temperatures.

As discussed earlier phenol can also be partially substituted with lignin for lignin based PF resin synthesis.<sup>111</sup> For example, 25% and 45% of the phenol used in an original PF sample was substituted with three different types of lignins (pine KL, soda anthraquinone flax lignin and sulphonated SKL). The  $T_g$  of all lignin based PF samples were then compared to the commercial PF resin. Three of the above-mentioned samples (45% soda anthraquinone flax lignin based novolac, 25% sulfonated SKL based novolac and 45% sulfonated SKL based novolac) showed a single  $T_g$ , positioned well between the  $T_g$ s of the pure lignin and the commercial PF resin samples. Surprisingly, the other samples showed two  $T_g$ s each indicating

the presence of a two-phase system. The lowest  $T_g$  was closer to the  $T_g$  of the commercially available novolac while the highest  $T_g$  was closer to the  $T_g$  of the used lignin. At this point it can be concluded that the long chain length and higher  $T_g$  of the lignin segment restricted the formation of a homogeneous system. It has also been documented that the time required for gelation during the crosslinking reaction (using hexamethylenetriamine as a crosslinking agent) was also strongly dependant on the molecular weight and chain length of the lignin.<sup>106</sup>

PF resins are well known for their adhesive applications in the plywood industries. For adhesive applications, the lignin should be of considerably low molecular weight since a higher molecular weight lignin would make the adhesive hard to permeate and the bonding strength could dramatically be reduced.<sup>112, 113</sup> As such in their effort to synthesize lignin based PF adhesives Jin and his group used enzymatic hydrolysis lignin (EHL), which had a comparatively low molecular weight (900 - 1300 g/mol). Up to 25% of the phenol was substituted with EHL. The fluidity of the bio-based PF adhesive was comparable to the commercial material, which made it easier to apply on the wood samples. The dry strength of the new material was seen not to change much with the substitution of phenol with lignin. However, the wet bond strength was found to improve significantly. The plywood created with this modified PF adhesive was also suitable for outdoor applications.<sup>112</sup>

50% of the phenol could be substituted with bagasse lignin to synthesize lignin based phenol formaldehyde resins for adhesive applications.<sup>114</sup> Thermal stability studies showed that the weight loss in the case of the lignin based PF resins was somewhat higher during the initial stage of the thermal decomposition (between 120 to 300 °C). This was attributed to the degradation of the lignin side chains. However, the thermal stability of lignin PF improved slightly compared to commercial phenol formaldehyde in the latter phases of the decomposition (between 300 to 600 °C) possibly implying that lignin formed stable three-dimensional structures with formaldehyde at elevated temperatures. DSC studies showed that despite the fact that the initiation of curing took place at a higher temperature for lignin based PF resins; the overall curing rate was higher than commercial PF resins. Earlier studies have also confirmed that the incorporation of lignin accelerates the phenol formaldehyde curing.<sup>115-116</sup>

Lignin obtained from different biorefinery residues (ethanol biorefinery residue, butanol biorefinery residue, xylitol biorefinery residue and lactic acid biorefinery residue) can also be used for the synthesis of bio based PF adhesives.<sup>117-118</sup> Notably, during biochemical reactions much moderate conditions are applied compared to the kraft process. As such the lignin obtained from such biorefineries are quite different to KL.<sup>117</sup> Comparing the adhesives synthesized from different biorefinery residues, Zhang and coworkers found that adhesives obtained from an ethanol biorefinery residue (ERPF) had a higher bond strength compared to a butanol biorefinery

residue (BRPF) and a xylitol biorefinery residue (XRPF).<sup>112</sup> Despite the fact that lactic acid biorefinery residue (LRPF) showed a higher bond strength than ERPF, its free phenol and formaldehyde content was higher than that of ERPF and the commercial PF.<sup>117</sup> The literature points towards the conclusion that lignin obtained from ethanol biorefinery residues was an excellent choice for the synthesis of bio-based PF resins.<sup>112</sup> However, it was also found that as the lignin content increased in ERPF, the thermal stability and bond strength of the end product reduced significantly. Overall 10% substitution with ERPF in a bio-based PF, created a material that had a thermal stability and bond strength very close to that of the commercial material.<sup>112</sup>

Lignin based resol (base catalyzed) resins have also been synthesized using organosolv pine lignin by Wanga et al.<sup>119</sup> They have shown that for smaller lignin contents, the temperature required to form the crosslinking was lower than that of the commercial material. This was mostly due to the phenolic hydroxyl rich structure of OSL. However, increasing the lignin content beyond 40%, a reduction in the rate of the crosslinking reaction was observed most likely due to the complex structure of lignin restricting its reaction with formaldehyde. An increase in the crosslinking temperature was necessary to complete the reaction. Similar to lignin-based novolacs, these materials also showed a reduction in thermal stability with an increase in the lignin content.

Grishechko et al. have shown that about 80% of the phenol could be substituted by SKL in the synthesis of lignin-phenol-formaldehyde based aerogels and hydrogels. However, these materials needed to improve their thermal insulation characteristics in order to be comparable with the commercial phenol-formaldehyde based aerogels.<sup>120</sup>

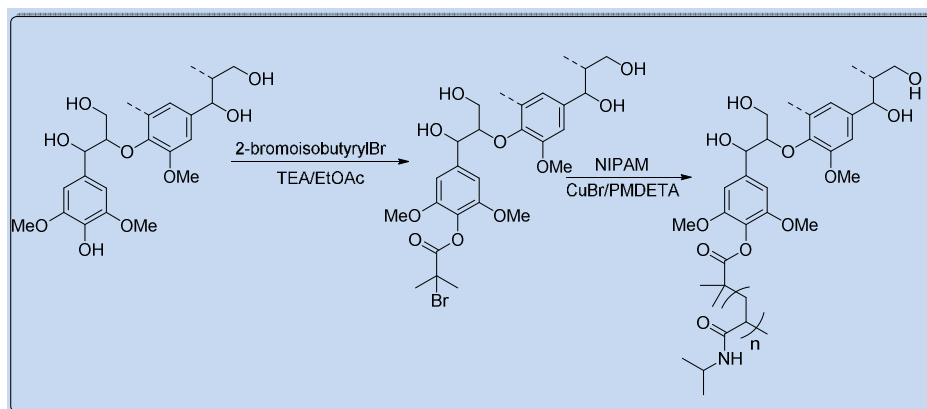
Lignins or bio-phenols are less reactive towards addition/substitution reactions due to the lack of reactive sites. However, the lignin extracted from pine sawdust by an organosolv-extraction allowed the substitution of phenol to produce viscous resol-type phenolic resins.<sup>121</sup> In the reported method, softwoods such as pine were found to be more advantageous over hardwoods and crop residues, since softwood lignin contains a higher content of G units, which are more active than S units. In this process when phenol was dominant, the thermal curing reactions were controlled by the reactivity of the phenol. However, when the lignin was the major component in the resin formulation, the thermal cure reactions were controlled by the lignin reactivity, which is much lower than that of phenol, resulting in slower cure

kinetics. TGA thermograms showed that with an increased lignin content in the resin's formulation both the average molecular weight and the polydispersity gradually increased due to the larger and non-uniform molecular weights of the lignins. However, the thermal stability, decomposition temperature, and carbon residuals were all significantly decreased.<sup>121</sup>

From the above discussion, it can be concluded that lignin can be successfully substituted with phenol (either partially or completely) in phenol formaldehyde resins. SKL showed the best results among different types of lignins examined. The incorporation of lignin compromises the thermal stability of the PF resin, which is mainly attributed to the superior thermal stability of commercial PF, resins compared to lignin itself. However, the curing of PF resins was found to be catalyzed by lignin inclusion and a drop in the curing temperature was also observed.

**Epoxidation.** Epoxy resins are comparatively low molecular weight pre-polymers which can be further crosslinked by either reacting with itself or an external curing agent (amines, acids, phenols, alcohols and thiols) to produce thermosetting polymers. Crosslinked epoxy resins are well known for their applications in electrical, electronics and automobile industries. These polymers are also widely used in adhesives; paints, carbon fiber, fiberglass composites and elastomer applications. However, bisphenol A, the main component used to synthesize epoxy resins possess some serious health issues.<sup>122</sup> Lignin or its hydroxyalkylated derivatives can be used as a substitute for bisphenol A for epoxy resin synthesis but it should be completely impurity free.<sup>103, 123-126</sup>

A comparative study of the thermal stabilities for three different types of lignin (wheat straw lignin, Sarkanda grass lignin, Protobind 100) based epoxy resins had been carried out by Malutan and coworkers. In this study the epoxidized resins were either directly synthesized from the natural polymer or synthesized from its hydroxymethylated derivatives.<sup>125</sup> The thermal stability experiments were conducted by heating the copolymer samples in a TGA instrument between 25 °C to 900 °C at a rate of 15 °C/min under a nitrogen atmosphere. The thermal stability of the epoxy resins synthesized from hydroxymethylated lignin was found to be marginally inferior compared to the epoxy resins synthesized from lignin itself. However, the amount of char residue remaining after the TGA measurements were slightly higher in the case of epoxy resins synthesized from the hydroxymethylated lignin.



**Scheme 11.** Synthesis of poly(N-isopropylacrylamide) grafted lignin reported By Kim and Kadla.<sup>127</sup>

Later Ding et al.<sup>128</sup> showed that the decomposition temperature of the lignin (alkali lignin and its formaldehyde derivative) based epoxy resins improved significantly compared to the commercially available epoxy resins when heated between 25 °C to 900 °C at a heating rate of 20°C/min. The aromatic structure of lignin had been held largely responsible for the additional improvements displayed in the thermal stability of this bio-based copolymer.

Lignin had also been used to synthesize epoxy resins by only partially substituting bisphenol A.<sup>129</sup> Lignin (obtained from bamboo by steam explosion) based epoxy resins were thus used to partially substitute bisphenol A creating bio-based epoxy resins. While this work demonstrated the tremendous potential of lignin, the thermal and mechanical properties of this material needed to be further improved so as to compete with the commercial material.

Lignin can be partially hydrolyzed to obtain comparatively lower molecular weight fragments with better solubility in organic solvents containing higher amounts of hydroxyl groups. Qin and co-workers reported their studies where they treated the partially hydrolyzed lignin with succinic anhydride to obtain lignin based polycarboxylic acids which were then further used as a crosslinking agent (along with synthetic acid anhydrides, like glycerol tris (succinate monoester) and hexahydrophthalic anhydride (HHPA)), for commercially available epoxy resins.<sup>130</sup> Their studies showed that both the  $T_g$  and the decomposition temperatures were reduced with increasing amount of lignin based polycarboxylic acids in the crosslinking agent. The better thermal properties of the epoxy resins cured with commercially available curing agents were mainly due to the rigid structures of these compounds and

higher crosslinking density. From the above discussion it is quite clear that lignin itself or its derivatives can successfully substitute bisphenol A for a lignin based epoxy synthesis. Lignin derivatives can also be used as crosslinking agents with commercially available epoxy resins. However, the thermal properties of these modified bio-based epoxy resins strongly depends on the structure of the lignin used initially.<sup>131</sup>

The introduction of lignin is an efficient method to produce low cost carbon fibers. Amongst different ways such carbon fibers have also been synthesized using free radical copolymerization of HKL with polyacrylonitrile (PAN) and spinning dope using a wet spinning process consisting of 16% of PAN-lignin copolymer in DMSO.<sup>132</sup> DSC studies of these fibers showed exothermic peaks at 285 and 308 °C respectively which clearly indicated that the lignin accelerated the oxidative stabilization reactions. The TGA analysis (up to 800 °C, with heating rates of 10 °C/min) showed the main mass loss being at around 280-450 °C due to the pyrolysis of the fibres.<sup>132</sup>

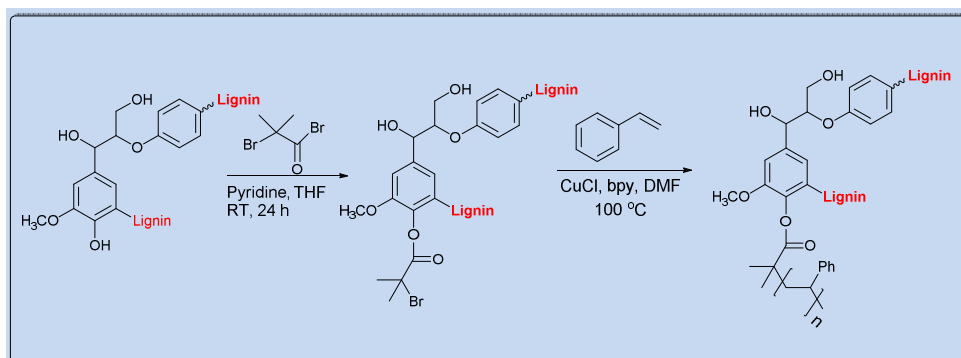
**Lignin grafted copolymer:** Synthetic polymer grafting on lignin opens up a new path in the field of engineering plastic materials.<sup>133</sup> By this method the properties of lignin can be tuned considerably. The grafted lignin copolymers can be used for different applications like paints and coatings, binders, flame retardants, water resistant composites, emulsifiers and biomedical applications.<sup>134-135</sup> Poly(N-isopropylacrylamide) is well known for its heat induced phase separation due to dehydration. Likewise the poly(N-isopropylacrylamide) grafted on HKL also shows thermoresponsive properties. This copolymer forms a clear solution at room temperature but precipitates out when heated at 32 °C.<sup>136,127</sup>





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Scheme 12. Synthesis of polystyrene grafted lignin.<sup>134</sup>

This behaviour is mainly attributed to the change in the structure of the *N*-isopropylacrylamide side chain depending on the temperature. At room temperature it remained in an extended form and was thus hydrophilic. With an increase in temperature it coiled up and attained a globular structure (by dehydration) and thereby became hydrophobic. DSC traces of the polymer solutions also showed an exotherm at 32 °C (which increased with an increase in the degree of substitution) supporting the phase change mentioned above. The authors also observed significant improvements in the Panesar *et al.* reported their effort regarding the synthesis of poly(vinyl acetate) grafted SKL copolymers.<sup>134</sup> The thermal stability of the grafted copolymer was slightly inferior to that of the pure polyvinylacetate. However, the  $T_g$  increased substantially after introduction of aromatic rich rigid lignin structures. Later, Chung and coworkers also reported an increase in the  $T_g$  of polylactic acid when grafted on SKL.<sup>138</sup> They described a 40 °C increase in  $T_g$  when lignin content was increased from 1-wt % to 50-wt %.<sup>138</sup> Recently Hilburg *et al.* described their work related to thermoplastic lignin nanocomposite synthesis. In this study the authors synthesized polystyrene and poly(methyl methacrylate) grafted lignin polymers through atom-transfer radical polymerization using a lignin microinitiator (Scheme 12).<sup>139</sup> They reported an increase in the  $T_g$ s (measured from the softening temperatures obtained by DMA) of the grafted polymers by 27 °C and 15 °C for the poly(methyl methacrylate) and polystyrene grafted lignins respectively compared to the corresponding homopolymers. This increase in the  $T_g$  can be attributed to the strong interaction between the synthetic polymer matrix and lignin. The higher increase in  $T_g$  in the case of poly(methyl methacrylate) grafted lignin copolymers can be described as a result of the stronger intermolecular interactions due to intermolecular hydrogen bonds.

thermal stability of the polymer with increasing degree of grafting. The decomposition temperature of lignin grafted with polyacrylic acid was also found to be increased by 32 °C compared to the starting lignin, though it showed initial weight loss due to anhydride decomposition.<sup>137</sup> At elevated temperatures, the acrylic acid component of the grafted copolymer melted and formed a protective coating on the lignin preventing it from heat conduction. As such an improvement in thermal stability was observed.

In order to create new lignin copolymers produced from SKL with controlled characteristics and increased thermal stability, a novel approach was used to systematically protect the phenolic hydroxyl groups of SKL and copolymerize it with 4, 4'-difluorodiphenyl sulfone (DFDPS). This method not only provided better thermal properties and uniform molecular weight distributions of copolymers but also provided a means for altering the properties of an otherwise intractable biopolymer.<sup>140</sup> Overall, lignin has been successfully copolymerized with different synthetic polymers. The thermal properties of these bio-based copolymers were found to be strongly depended on the lignin used for the procedure. However, some of the superior thermally stabilized polymers show reduction in thermal stability as a result of lignin incorporation. The bio-based copolymers can either form a single phase or a multi phase copolymer depending on the compatibility of the lignin segment with the commercial polymer segment. As such a single or two different  $T_g$  can be observed for various systems.



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$$T_{gm} = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} + \frac{A w_1 w_2}{(w_1 + k w_2)(w_1 + b w_2)(w_1 + c w_2)^2} \quad \text{A}$$

$$k = \frac{\Delta c_{p2} - w_1 \delta c_p^l}{\Delta c_{p1} - w_2 \delta c_p^g}, A = \frac{-\chi R(T_{g1} - T_{g2})c}{M_1 \Delta c_{p1}}$$

Where  $T_{gm} = T_g$  of the binary polymer blend,  $w_i$  = the weight fraction of the  $i$ th component,  $T_{gi}$  = the  $T_g$  of the  $i$ th component,  $b = M_2/M_1$  ( $M_i$  = molecular weight per chain segment of polymer  $i$ ),  $c = \rho_1/\rho_2$  ( $\rho_i$  = density of the  $i$ th polymer)  $c_{pi}$  = isobaric specific heat of the  $i$ th component,  $\Delta c_{pi} = (c_{pi}^l - c_{pi}^g)$  at  $T_{gi}$ , where 1 and g denotes the liquid and the gas phase respectively.<sup>141</sup> However, the intermolecular interactions of the polymers strongly control the  $T_g$  of the blend. According to Lu Weiss equation, a negative deviation from linearity is an indication of weak specific intermolecular interaction.<sup>141</sup> In this case the  $k$  value is greater than the value of  $A$ . As such the Lu Weiss equation can be simplified as shown below which is known as the Gordon-Taylor equation.<sup>58</sup>

$$T_{gm} = \frac{w_1 T_{g1} + K w_2 T_{g2}}{w_1 + K w_2} \quad \text{B}$$

where  $K = k + A/(T_{g2} - 1)$ . Here  $K$  is designated as a measure of intermolecular interaction between the polymer molecules. On the other hand, when the constituent polymers show strong intermolecular interaction  $A$  is much larger than  $k$ ,  $b$  and  $c$ . Thus Lu Weiss equation can be approximated as shown below which is known as Kwei's equation.<sup>142</sup>

$$T_{gm} = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} + A w_1 w_2 \quad \text{C}$$

where  $k = \frac{\Delta c_{p2}}{\Delta c_{p1}}$  and  $A$  denotes the measure of intermolecular interaction of the polymers. As such a single composition dependent  $T_g$  of the blend signifies the miscibility of the polymers at a molecular level.<sup>143</sup>

Equation 1. A) Lu Weiss equation B) Gordon-Taylor equation C) Kwei's equation

**Lignin polymer blends:** Polymer blends can either be miscible or immiscible. Overall, miscibility of two polymers is in general entropically unfavourable unless the polymers involved possess some form of intermolecular interaction. This makes the enthalpy of mixing sufficiently negative to overcome the opposing entropic considerations.<sup>143</sup> The  $T_g$  of a polymer blend depends on the type of intermolecular interaction of the component polymers. In a binary polymer blend if the two components are completely miscible the blend shows a composition dependent  $T_g$ . If the polymers are compatible with each other but not completely miscible, two different  $T_g$ s can be observed depending on the composition of the blend. However, if the two polymers of a binary blend are immiscible with each other, the resultant blend shows two different  $T_g$ s which are very close to the  $T_g$ s of the starting polymers and those do not change with a change in composition.<sup>144</sup> In the case of miscible and compatible blends and depending on the strength of the intermolecular interactions of the component polymers, the  $T_g$  varies.

In short The  $T_g$  of a polymer blend depends on the  $T_g$  of each component of the blend, the weight fractions of the individual component of the blend and the thermodynamics of the intermolecular interactions between them.<sup>58, 141-142, 145-147</sup> In an effort to unify these variables Lu and Weiss proposed an empirical formula (equation 1A) to express the  $T_g$  of a binary polymer mixture.<sup>45, 141</sup>

Lignin can be blended with other synthetic polymers in two ways, either alone or after derivatization through chemical modifications. The  $T_g$ s of the resultant blends vary depending on the intermolecular interaction between lignin or the lignin derivative and the other polymer.

The blending of SKL with synthetic polymers has been used to prepare a better thermoplastic lignin based material.<sup>11</sup> Also, the alkylation of KL has been used to modulate its thermal and chemical reactivity. Sarkanen et al. reported the blending of alkylated KL with aliphatic polyesters.<sup>148</sup> The alkylated KL functioned as a plasticizer. As a result a distinct reduction in



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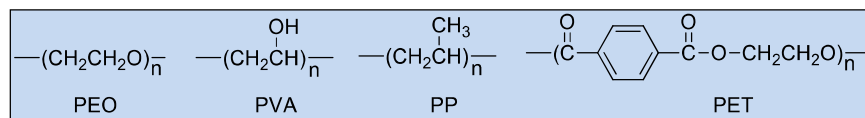


Figure 4. Synthetic polymers used to make lignin blends by Kadla and Kubo.<sup>133</sup>

the  $T_g$  was observed. Generally, the preparation of miscible polymer blends depends on the exothermic interactions between the components being mixed. The blend composition affects the  $T_g$  because of the varying intermolecular interactions.<sup>148</sup> They also observed that the miscible low- $T_g$  polymers are more efficient when their interactions with the alkylated KL components are minimized.<sup>149</sup> For example, acylated lignins are plasticized using poly(ethylene glycol), but the blends are less compatible than those of their alkylated counterparts.<sup>149</sup> In 2011, Chen and coworkers reported their research work regarding the thermal properties of lignin and dodecyl lignin along with their respective polypropylene blends. The authors examined the thermal degradation of the polymer blends by TGA in the temperature range 100 °C to 600 °C using 20 °C/min heating rate under a nitrogen atmosphere.<sup>150</sup> The thermal stability of the lignin polypropylene (PP) blend was found to be better (irrespective of the fact that underivatized lignin or alkylated lignin had been used for the blend preparation) than the natural polymer itself. This was attributed to a synergistic effect originating from the charring of the lignin and the hydrocarbon radicals formed from polypropylene during the thermal degradation. The char yield was also seen to increase with an increase in the weight fraction of lignin present in the blend. The authors also found that the polymer blend made from alkylated lignin had a marginally better thermal stability compared to the underivatized lignin (10% weight loss occurred at 200 °C for the underivatized lignin sample while it occurred at 215 °C for the alkylated lignin). However, due to the presence of higher weight fraction of aromatic groups, underivatized lignin showed a higher amount of char yield (60%) while the alkylated lignin showed comparatively lesser amount of char yield (45%).<sup>150</sup> The incorporation of the long chain dodecyl group on the lignin makes it more compatible with PP, which in turn is reflected in the better thermal stability of the alkylated lignin PP blend.

Sadeghifar and Argyropoulos have recently shown that the phenolic hydroxyl groups play an important role toward imparting antioxidant properties in lignin.<sup>151</sup> Using fractionation and methylation studies on KL it was observed that the acetone soluble KL displayed considerably augmented

antioxidant characteristics than its methylated derivative. More specifically, it was shown that selectively masking the phenolic groups the antioxidant properties of KL was modulated. Methylation was also shown to affect the thermal stability of its blends with polyethylene (PE) reducing the thermal degradation temperature of PE significantly by using oxidation induction temperature (OIT) measurements.

High-density polyethylene (HDPE) is a nonpolar hydrocarbon based synthetic polymer. Hence it is expected that HDPE would form an incompatible blend when mixed with lignin. The melting temperature of HDPE deviated slightly on blending with 10-weight % of straw lignin and remained almost unchanged on increasing the amount of lignin to 20-weight %.<sup>152</sup> The DMA data actually showed no change in  $T_g$  (-115 °C) of HDPE upon blending with lignin (10 % w/w) even on increasing the amount of lignin to 20 % w/w.<sup>152</sup> As anticipated the unaltered melting temperatures and  $T_g$ s were most likely due to the immiscibility of HDPE and lignin. Similar results were also obtained when nonpolar amorphous polystyrene was blended with straw lignin.<sup>152</sup>

The interactions of lignin with different polar and nonpolar synthetic polymers were examined in efforts where the authors blended HKL with different synthetic polymers.<sup>143</sup> More specifically lignin blends with poly(ethylene oxide) (PEO), poly(ethylene terephthalate) (PET), PP and poly(vinyl alcohol) (PVA) (Fig 4) have been studied<sup>143</sup>. The lignin/PEO and lignin/PET systems showed a single, composition dependent,  $T_g$ , which decreased with increasing amount of synthetic polymer in the blend indicative of complete component miscibility. In both cases, the strong hydrogen bonds between the hydroxyl groups of lignin and the ether groups (for the case of PEO) and carbonyl groups (for the case of PET) promoted polymer miscibility.<sup>44</sup> The change in the  $T_g$  in the lignin/PEO system was found to be more prominent than in the lignin/PET system. Using the Lu Weiss equation (Eq. 1, A), the authors showed that the effect of  $k$  exceeded the effect of  $A$  while in the case of lignin/PEO system the effect of  $A$  exceeded the effect of  $k$ . These data suggest that despite the fact that both PEO and PET possess proper functional groups to form hydrogen-bonds with lignin, the intermolecular

interactions between lignin and PEO are stronger than lignin and PET. As such a higher reduction in the  $T_g$  was observed in the case of the lignin/PEO system. These contentions were also supported with independent FT-IR data.<sup>143</sup>

Lignin/PP and lignin/PVA blend systems showed two separate  $T_g$ s indicating the presence of a two-phase system. Being nonpolar PP does not offer sufficient intermolecular interactions with the polar lignin resulting in immiscible polymer blends.<sup>143</sup> However, it has been shown that there are strong intermolecular interactions (hydrogen bonds) between lignin and PVA.<sup>153</sup> Despite this, these two polymers were found to be immiscible, however, no rationalization was offered. One possibility could be that the crystalline regions of PVA generated due to strong intra and intermolecular hydrogen bonds may have restricted its proper mixing with lignin. In another effort Kubo and Kadla showed that the phenolic hydroxyl groups of lignin contributed more towards intermolecular hydrogen bonding compared to the aliphatic hydroxyl groups.<sup>154</sup> This is understandable due to the higher acidity of the phenolic hydroxyl groups. In the same report the authors discussed the thermal properties of PEO lignin and methylated lignin blends respectively. Both systems showed single, composition dependent  $T_g$ s due to the complete miscibility of the polymers with the homogeneous amorphous phase. However, upon examination the authors found that the polymer-polymer interaction factor for the lignin-PEO blends was higher compared to that of the methylated lignin-PEO systems. As the phenolic hydroxyl groups of the methylated lignin were completely masked by methylation, their propensities to form inter and intramolecular hydrogen bonding reduced dramatically. As such the intermolecular interaction between HKL and PEO was higher than that of the methylated derivative. This was also reflected on the A values of the systems. HKL/PEO blends showed a higher A value compared to methylated HKL/PEO blends (A of HKL/PEO = -170 and A of methylated HKL/PEO = -193) pointing out to the former having a higher tendency to form intra and intermolecular hydrogen bonds.<sup>154</sup> On the other hand, methylated HKL showed higher molecular mobility (since the intermolecular hydrogen bonds were eliminated) compared to HKL as indicated by their respective  $T_g$ s. HKL showed a  $T_g$  of 106 °C while methylated HKL showed a  $T_g$  of 86 °C. As such, despite the fact that the methylated HKL showed lower intermolecular interactions with PEO the reduction in the  $T_g$  in the methylated HKL/PEO blend was comparable to that of HKL/PEO system. Blends of 75 % (w/w) of HKL and 25 % (w/w) PEO showed a 68 °C reduction in the  $T_g$  compared to pure HKL, while blends of 75 % (w/w) methylated HKL and 25% (w/w) PEO showed a 73 °C reduction in  $T_g$  compared to methylated HKL. It can therefore, be concluded that the  $T_g$  of a blend primarily depends on the miscibility (intermolecular interactions) of its components. However, it is also dependent on the molecular environment and the nature of the component polymers.

In other efforts, Kubo and Kadla examined the interaction of different types of lignins namely OSL, HKL and SKL with PEO and compared their degrees of interaction and the ensuing changes in the  $T_g$ s.<sup>143, 155-156</sup> In all cases the DSC thermograms (scanned between -90 °C to 200 °C at a heating rate of 20 °C /min) a single compositional dependent  $T_g$  for each blend was evident based on the actual mixing efficiency of the polymers at a molecular level. Overall, the Gordon-Taylor and Kwei equation (Eq. 1, C) provided a good fit for all three types of lignin blends with PEO. Using additional computations, the authors showed that among the three different types of lignin OSL had the greatest propensity to form intermolecular interactions with PEO since the A value for this system was (-147) compared to HKL (-170) and SKL (-269). The strength of the intermolecular interactions of OSL and HKL were the same as both showed the same k value (0.37), while SKL showed a smaller k value (0.27). The greater interaction between OSL and PEO was attributed to its ability to form more intermolecular hydrogen bonds. Despite the fact that OSL and HKL contained approximately the same amounts of phenolic hydroxyl groups (4.3 mmol/g), which was somewhat higher to those present in, SKL (3.8 mmol/g), OSL had a higher amount of ketone groups. This was considered by the authors as pivotal in augmenting its interactions with PEO.

On the other hand SKL is a more condensed (sterically hindered) structure compared to OSL and HKL. As such, its interaction with PEO was the least. This was also supported by the calculated interaction energy density values.

The above effort and knowledge was then applied towards creating effective lignin-synthetic polymer blend systems aimed at carbon fiber preparation. Due to immiscibility and the ensuing phase separation, the lignin-PP blends formed hollow core fibers. SEM analyses showed the presence of pores both on the surface and the core of the carbon fibers made from lignin-PP blend.<sup>157-158</sup> On the other hand, no pores were observed for carbon fibers generated from lignin-PET blends since the two polymers were completely miscible.<sup>157</sup> Young's modulus and elongation at break of the carbon fibers prepared from lignin-PP blends containing 5 % (w/w) of PP were comparable to that of the carbon fibers made from lignin itself. However, the mechanical properties dropped dramatically with an increase of the PP content in the blend.<sup>157</sup> Increasing the amount of PP created more pores in the material, which certainly resulted in the deterioration of the mechanical properties. The tensile strength and the modulus of the carbon fibers generated from lignin-PET blends (95% (w/w) lignin) were comparable to that of the lignin homofiber and improved with increasing PET content.<sup>157</sup>

In their earlier work, Kadla and Kubo showed that PEO formed the best blends with lignin and good fibers were generated from HKL/PEO and OSL/PEO blends while SKL/PEO blends could not form fibers.<sup>159</sup> Due to its condensed structure SKL/PEO blends required a higher temperature to mix, which was higher than its degradation temperature. Overall the spinability of the lignin-PEO blends was found to be better than the lignin homofiber. However, since OSL is of a lower  $T_g$

the fibre spun from OSL/PEO blends were unstable during the carbonization step. Only HKL/PEO blends (95 % (w/w) HKL were able to form carbon fibers. Notably, above 5% (w/w) PEO, the system became thermally unstable. The resulting carbon fibres showed comparable tensile strengths and modulus with the lignin homo -fibre. Unfortunately, these values were seen to reduce with increasing amounts of lignin.<sup>159</sup>

Poly(L-lactic acid) (PLLA) is a semi-crystalline biodegradable polymer with the melting point of the crystalline phase being at 169.9 °C and the  $T_g$  of the amorphous phase at 63.4 °C. Hence it has potential to form a completely green system when blended with lignin. In this context Li *et al.* described their efforts on PLLA blends.<sup>160</sup> The high crystallinity of PLLA is responsible for its poor processing ability. As such PLLA was mixed with different proportions of hardwood lignin manually and moulded in a compression press at 200 °C. The blends showed a distinct reduction in both  $T_g$  and the melting temperature indicating the presence of strong intermolecular interaction between the two polymers. These reductions increased with an increase in the amount of lignin present in the blend. However, the authors were unable to determine the initial  $T_g$  of the hardwood lignin sample. FT-IR studies of the blends clearly showed the presence of intermolecular hydrogen bonds between the phenolic hydroxyl groups of lignin and the carbonyl oxygen of PLLA, which was attributed as being responsible for the formation of a miscible blend and the observed reduction on  $T_g$ . The tensile strength and elongation at break decreased dramatically with an increase in the lignin content in the blend. However, the modulus of the blend remained comparable to the starting PLLA sample up to 20% (w/w) lignin incorporation.<sup>160</sup> Despite the fact that the mechanical properties of the blends deteriorated dramatically with the incorporation of lignin the ease of processing encouraged the authors to create low lignin containing blends (20% (w/w) lignin).

Similar to lignin, lignin derivatives can form thermoplastic blends with synthetic polymers. Among various lignin derivatives blends of lignin esters with synthetic polymers have been extensively studied. Fully substituted OSL esters can form miscible blends with PCL with miscibility strongly depending on the number of carbons present in the ester side chain.<sup>161</sup> The blends of OSL acetate (OSL-Ac), propionate (OSL-Pr), butyrate (OSL-Bu) and valerate (OSL-Va) have been examined.<sup>161</sup> DSC thermograms showed that the OSL-Ac/PCL system was not particularly miscible, with the blend being immiscible when the amount of OSL-Ac was increased to 50% (w/w). On the other hand OSL-Pr/PCL, OSL-Bu/PCL and OSL-Va/PCL blends showed a single, composition dependent,  $T_g$  which generally increased with an increase in the lignin ester content of the blend.<sup>161</sup> It can thus be concluded that the miscibility improves with an increase in the chain length of the ester group. As the phenolic hydroxyl groups were completely masked by esterification no hydrogen bond interactions were observed via FT-IR spectral studies. As the chain length of the

ester side group was extended, the structural similarity between lignin esters and PCL increased. This was rationalized on the basis that the highly crystalline nature of PCL was disrupted with the incorporation of variable chain length esters. As such the OSL-Va/PCL and OSL-Bu/PCL blends showed better miscibility compare to OSL-Ac and OSL-Pr/PCL. Mechanical property studies showed that all blend samples had inferior tensile strength, modulus and elongation at break compared to the starting PCL, but improved as the chain length of the ester side group increased.<sup>161</sup> Overall, blending of lignin with synthetic polymers provides a powerful and convenient pathway to generate new materials with improved property/cost performance.<sup>162</sup> Since most blended polymers are immiscible, efforts towards promoting compatibilization are required to obtain maximum synergy.

The addition of low-molecular-weight compounds that may function as actual compatibilizers was examined in conjunction with the creation of covalent crosslinking.<sup>163</sup> Zhong and Sun have reported of blends of MDI, soy protein isolates (SPI), polycaprolactone (PCL),<sup>164</sup> and poly(ethylene-co-ethyl acrylate-co-maleic anhydride).<sup>165</sup> All these compatibilized blends exhibited lower water absorption. The SPI/PCL blend compatibilized with 2% (w/w) MDI showed maximum values of tensile strength, elongation at break, Young's modulus, and toughness. Furthermore, Huang *et al.* reported that the blends of SPI, KL and MDI resulted in improving the strength properties of the ensuing material.<sup>166</sup> Endothermic peaks observed via DSC studies apparent in the low temperature range of 88 to 77°C were attributed to the glass-transition temperature of SPI plasticized with GL ( $T_g$ 1). It was suggested that the formation of graft copolymers and crosslinked structures (promoted via the reactivity of MDI) increased the chain entanglements among the components and hence improved miscibility.<sup>166</sup>

Lignin is considered as suitable filler for polymers due to its abundance, low cost, low density, high thermal stability and high reactivity. These qualities make it better filler compared to other organic and inorganic alternatives. Furthermore, the incorporation of lignin could synergistically add to the polymer's cost effectiveness, biodegradable characteristics, thermal and photo stability.<sup>167</sup> Recent published data has shown that the self -association of lignin also affects the thermal properties of polymer and its blends with it.<sup>168-169</sup> Recently, the effect of KL on protein aggregation was reported by Sakunkittiyut and co-workers. Fish protein powder was blended with 30% glycerol and 0–70% (w/w) KL. Then, these blends were thermo-formed by moulding. The addition of KL increased the protein solubility and the mechanical properties of the material while it decreased its water absorption. It also resulted in a decrease in the viscosity of the protein blends as determined by capillary rheometry. KL was thus suggested as a suitable alternate additive for the enlargement of the protein thermal processing window.<sup>170</sup>

Polystyrene blends with KL and the associated changes caused by chemical modifications of it were studied by Lisperguer and his group.<sup>171</sup> KL was obtained from *Eucalyptus globulus* and *Eucalyptus nitens*. The lignin was isolated by acid precipitation and chemically modified using maleic anhydride. This lignin and derivatives were then incorporated into recycled PS at 2, 5, and 10% (w/w) using a melt-blending process. DSC measurements showed that the  $T_g$  values of the blends were higher than those of the virgin PS. Furthermore; TGA studies revealed minor improvements in the thermal stability of PS when lignin was incorporated at low levels.

At this point it can be concluded that the mutual interaction and miscibility of the component polymers governs the  $T_g$  of the polymer blend. Synthetic polymers containing polar groups offer the possibility of creating intermolecular hydrogen bonds with lignin while nonpolar synthetic polymers generally form immiscible blends which show two distinct  $T_g$  for the two immiscible phases.<sup>172</sup>

**Lignin synthetic polymer composites:** Polymer composites are generally obtained by reinforcing either a natural or synthetic polymer matrix with reinforcing synthetic (glass, carbon) or natural (hemp, flax, pine needles, lignin, bagasse etc) fibres or particles.<sup>20, 173-175</sup> Due to their superior mechanical strength, durability and light weight, polymer composites are widely used for aerospace, automotive, military, sports and constructions applications.<sup>176</sup> To this effect, lignin has been explored used as a reinforcing material within a synthetic polymer matrix for composite preparation.<sup>177</sup> In their studies Barzegari and co-authors prepared PS lignin composites with varying contents (20%, 40%, 60%, 80%) of Indulin lignin (SKL) by the process of melt mixing.<sup>178-179</sup> While PS is an aromatic rich amorphous polymer (similar to lignin) the polarity differences between them make them only partially compatible with each other. The compatibility, however, was seen to increase with an increasing amount of lignin in the mixture.<sup>180</sup> TGA studies showed that the thermal stability of the composite material improved significantly irrespective of the lignin content. The presence of free radical quenching functional groups in lignin has been invoked as the reason for its antioxidant thermal stabilizing abilities.<sup>40, 181</sup> As such lignin prevented the thermal degradation of polystyrene (mainly caused by freed radical degradation) in the composite and improved the thermal stability in the thermoplastic.<sup>178</sup> DSC thermograms of the material showed a single  $T_g$ , close to that of pure lignin. DMA studies of the composite material showed that the mechanical property improved with the introduction of lignin in the polystyrene matrix. The storage modulus increased from 1.24 GPa to 2.25 GPa when 80% (w/w) lignin was introduced. At higher temperatures PS showed a sharp reduction in its storage modulus and this was also reflected in the storage modulus of its blends with KL. The storage modulus was also found to be increased with increasing content of lignin as a result of increasing chain entanglement. Hence, the incorporation of lignin in PS composites not only improved the thermal stability of polystyrene but it also

improved its viscoelastic properties. In early 2000, Thielemans and Wool reported their work regarding the preparation of thermoset composites using KL fibers and acrylated epoxidized soybean oil/styrene (AESO/styrene) polymer matrices.<sup>182-183</sup> In this study the authors modified the lignin through esterification so as to make it more compatible with styrene. They found that lignin butyrate showed the best solubility with styrene but acetylated, methacrylated and propionated lignins showed partial solubility. Incorporation of lignin derivatives in the polymer matrix showed two effects. In the case of densely cross-linked material, butyrate lignin improved the mechanical properties of the composites while in the case of less densely crosslinked substances butyrate lignin acted as a plasticizer.

Averous et al. have explored the mechanical and thermal properties of bio-composites whose main matrix was the biodegradable copolymer polybutylene adipate-co-terephthalate (PBAT) with lignocellulose fillers arising from an industrial fractionation process using wheat straw. The addition of the lignocellulosic fillers was found to provide a slight increase in the  $T_g$  of the matrix most likely due to intermolecular interactions between the filler's hydroxyl groups and the carbonyl groups of the PBAT ester. Such interactions would likely reduce the polymer mobility which will be reflected in augmented  $T_g$  values.<sup>184</sup>

In a number of instances the differences in polarity between lignin and nonpolar polyolefins has been held responsible for the weak mechanical properties of its composites with PE and PP.<sup>185-187</sup> However, in their studies, Sahoo et al. showed that a commercial lignin based material; Arboforam F 45 (55% alkali lignin obtained from the paper industry and 45% ground plant particles like hemp, flax, wood chips) is compatible with the polar polymer polybutylene succinate (PBS).<sup>188-189</sup> DSC studies showed that the  $T_g$  of the composite materials increased with increasing lignin content. This was attributed to strong positive interactions occurring between the polymer matrix and the lignin based fillers. The formation of physical crosslinking through the generation of strong hydrogen bonds between the lignin hydroxyl groups and carbonyl oxygens of PBS established restrictions on the segmental motion of the polymer chains. As such an increase in the  $T_g$  was observed. Conversely, samples loaded with 65% (w/w) lignin filler showed two distinct  $T_g$  corresponding to the polymer matrix and biomaterial filler respectively. The higher loading of lignin, was thought to have been responsible for the apparent phase separation observed within the composite. The authors also observed an increase in the storage modulus of the composite compared to pure PBS. They also demonstrated that the high thermal stability (measured by TGA) of PBS (degradation onset 306.4 °C) was somewhat compromised by the addition lignin filler whose onset of degradation was at 179 °C. The composite was also found to be generating a great amount of char after being heated in the TGA for up to 600 °C. This characteristic pointed out that the incorporation of lignin could improve the flame retardancy of the composite.

The effort reported by Canetti and Bertini<sup>190</sup> showed that the high thermal stability of PET was compromised in a composite containing 20% (w/w) hydrolytic lignin. However, the authors also showed that when the thermal stability was examined in an atmosphere of air the lignin was oxidized to form a carbon rich char coating on the composite material. As such air cannot enter the bulk of the composite material and consequently the reduction in the molecular weight via thermal degradation pathways was found to be significantly lower.

The curing agents used with epoxy resins (amines and acids) have recently been documented as being toxic posing specific health hazards. As such in their article Khalil and his group showed that the phenolic hydroxyl groups of lignin can offer to it the characteristics of a green curing agent for epoxy resins hardening it in various composite applications.<sup>191</sup> The authors used lignin obtained from soda-anthraquinone black liquor produced from the pulping of the fiber of oil palm empty fruit. This study showed that the initial thermal stability (measured by TGA) of the epoxy cured with lignin (onset decomposition temperature 239 °C with 15% lignin incorporation) improved significantly compared to the thermal stability of the epoxy cured with amine (onset decomposition temperature 152 °C). In contrast, amine-cured lignin showed better heat resistance compare to lignin-cured epoxy at elevated temperatures. 50% weight loss of amine-cured lignin took place at 389 °C while the same weight loss temperature for lignin-cured epoxy varied between 345 °C to 363 °C. The increase in the crosslinking density in amine-cured epoxy was used to rationalize its higher thermal stability. Increasing the lignin content showed higher onset decomposition temperatures. However, beyond 25% (w/w) lignin the thermal stability gradually deteriorated. Therefore an optimum lignin loading was found to be essential for thermal. Subsequently, Yin et al. also showed that lignin (enzymatic hydrolysis from corn straw) could be used as a curing agent for epoxy resins. Not surprisingly, the curing temperature of the epoxy resin was found to reduce significantly in the presence of an amine curing agents.<sup>192</sup> For example, epoxy resins could be cured at 174 °C when mixed with 1 equivalent of lignin, while the curing temperature reduced to 110 °C when 0.5 equivalents of polyamine was added to the epoxy lignin system.

Biocomposites based on a ternary system containing SKL (Indulin AT), PLLA and PEG have also been reported.<sup>193</sup> The effects of composition on the overall thermal properties of PLLA/PEG systems were investigated using DSC and TGA. It was evident that varying the amount of PEG as well as their molecular weight did not significantly affect the melting point ( $T_m$ ) of the PLLA phase. On the other hand, a slight decrease in the  $T_m$  of the PEG phase was observed for higher molecular weight PEG. Moreover, the crystallinity of the PEG phase showed a composition-dependent behaviour since the enthalpy of fusion for the PEG phase increased with increasing its content in the blends.<sup>193</sup>

Kosikova et al. studied the sulfur-free lignin derived from the methanol-based organosolv pulping of spruce wood.<sup>194</sup> To

elucidate the effect of lignin, the tensile strength and elongation at break of polypropylene films containing 2-10% (w/w) of spruce OSL and/or beech wood pre-hydrolysis lignin were compared with lignin-free polymers.<sup>194</sup> The interaction of PP with lignin became evident from the comparison of differential thermal analysis (DTA) curves of pure PP and PP containing 2% (w/w) lignin. The latter was shown to exhibit an exothermic peak starting at 200°C. The presence of this peak in DSC thermograms of lignin-modified PP was attributed to a chemical interaction between PP and lignin occurring during the thermal processing of the composite blend.<sup>194</sup>

Styrene butadiene rubbers (SBR) are well known for their applications in tire, construction, and shoe industries. Carbon black is often used as reinforcing filler during the compounding of SBR. However, carbon black has some documented health issues with its main source being petrochemically based. In efforts to locate an alternative for this reinforcing filler, Xiao et al. used lignin along with layered double hydroxide (LDH) formed by magnesium nitrate and aluminum nitrate.<sup>195</sup> Thermal properties studies showed that the  $T_g$  of LDH-lignin filled SBR remained unchanged from pure SBR. Surprisingly, the authors report that the  $T_g$  did not change with variable amounts of lignin in the rubber, which maintained its elastic properties. TGA studies showed that at 10 % (w/w) lignin content the thermal degradation temperature of LDG-lignin filled SBR was lower than that of pure SBR. This was due to the lower thermal stability of the lignin compared to SBR. However, a 50 % (w/w) lignin contents the degradation temperature of LDG-lignin filled SBR was almost 11 to 18 °C higher than that of pure SBR. At higher temperatures the dispersion of LDG-lignin in the SBR matrix was much better. This formed a protective barrier on the polymers restricting the release of the volatile materials formed during the degradation.

Recently El-Zawawy et al. reported their studies regarding the formation of lignin (obtained from the black liquor of alkaline pulping of rice straw) and Co(II) lignin complexes used in filled PS composites.<sup>196</sup> As per previous efforts the lignin was found to be compatible with PS since DSC showed a single  $T_g$ . The compatibility improved further when a lignin Co (II) complex was used as the filler. The polarity of the lignin sample was found to be reduced as the bare hydroxyl groups complexed with  $Co^{2+}$  ions. A  $T_g$  closer to pure PS confirmed the better compatibility of lignin Co(II) complex with PS. Stiubianu and his group has shown that although lignin displays some interactions with polysiloxane, in a composite of a polysiloxane matrix filled with lignin, the biopolymer itself did not affect the thermal behaviour of the polymer.<sup>197</sup>

At this point it is reasonable to conclude that the lignin can be used as a reinforcing material along with a synthetic polymer matrix for composite applications. The chemical structure and physical properties of the used lignin in the creation of the composite strongly influence the properties of the end product.

## Conclusions

This effort offers a comprehensive overview of the thermal properties of lignin-based copolymers, blends and composites. The chemical structure and physical properties of the starting lignin considerably influences the thermal properties of these bio-based materials. Due to its aromatic rich structure, lignin generally improves the thermal stabilities of copolymers, blends and composite materials with a few exceptions. The phenolic hydroxyl rich structure of lignin offers the possibility to create intermolecular hydrogen bonds with polar polymers containing electronegative groups. This intermolecular interaction not only helps the lignin to be compatible with polar synthetic polymers but also influences the  $T_g$ . Generally an increase in the  $T_g$  is observed when lignin is treated with other polar synthetic polymers as a result of intermolecular hydrogen bonds. Its rigid aromatic rich structure also contributes towards augmenting  $T_g$ s. Lignin usually forms incompatible systems when mixed with a nonpolar synthetic polymer, hence the clear presence of multiple phases is observed. Such binary systems generally show two separate  $T_g$ s for their respective phases.

Recent advances in the field of biopolymer processing are highly promising for the design of sustainable, low cost materials. Rational next steps in sought developments need be focused in facile methods that offer effective lignin fractionation, facile chemical modifications and copolymerization techniques. All of the above need be coupled with detailed evaluations of the polymer and other physicochemical characteristics of these materials. These efforts may propel further our knowledge of effectively modulating the thermal and processing characteristics of lignin its blends and its copolymers via cost effective and environmentally sustainable technologies.

## Abbreviations

AQ- Flax- Anthraquinone Flax  
 BRPF- Butanol biorefinery residue  
 CEM- Complex electric modulus  
 CL-  $\epsilon$ -caprolactone  
 DMSO- Dimethyl sulfoxide  
 DSC- Differential Scanning Calorimetry  
 EHL- Enzymatic hydrolysis lignin  
 ERPF- Ethanol biorefinery residue  
 HBPEA- Highly branched poly(ester-amine)s  
 HDI- Hexamethylene diisocyanate  
 HDPE- High-density polyethylene  
 HHPA- Hexahydrophthalic anhydride  
 HKL- Hardwood kraft lignin  
 SKL- Softwood kraft lignin  
 KL- Kraft lignin  
 KLCL- Kraft lignin polycaprolactone copolymers  
 LOAP- Lignin/oleic acid macro polyol  
 LPU- Lignin based polyurethanes  
 LRPF- Lactic acid biorefinery residue

MDI- Methylene diphenyl diisocyanate  
 OSL- Organosolv lignin  
 OSL-AC- Organosolv lignin acetate,  
 OSL-Bu- Organosolv butyrate  
 OSL-PR- Organosolv Propionate,  
 OSL-Va Organosolv valerate  
 PBD- Polybutadiene  
 PCL- lignin-based polycaprolactone  
 PEG- Polyethylene glycol  
 PEO- Poly(ethylene oxide)  
 PEO-Lignin-poly(ethylene oxide)  
 PET- Poly(ethylene terephthalate)  
 $T_g$ - Glass Transition Temperature  
 PLLA- Poly(L-lactic acid)  
 PP- Polypropylene  
 PU- Polyurethane  
 PVA- Poly(vinyl alcohol)  
 SBR- Styrene Butadiene Rubber  
 SL- Softwood lignin  
 $S_NAr$ - Substitution nucleophilic aromatic  
 SPI- Soy protein isolate  
 TDI- Toluene diisocyanate  
 TDI-HTPB-2,5-toluene diisocyanate-hydroxy terminated polybutadiene  
 TGA- Thermogravimetric analysis  
 THF- Tetrahydrofuran

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## Graphical Abstract

**Thermal Properties of Lignin in Copolymers, Blends, and Composites**Sanghamitra Sen<sup>‡</sup>, Shradha Patil<sup>‡</sup>, Dimitris S. Argyropoulos<sup>‡,§,\*</sup>

Modulating thermal properties via lignin copolymers, blends, and composites.

